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EPA/IERL-RTP Procedures Manual Level 2 Sampling and Analysis of Oxidized Inorganic Compounds

TRW Defense and Space Systems Group
Redondo Beach, CA

Prepared for

Industrial Environmental Research Lab.
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EPA/IERL-RTP Procedures Manual: Level 2 Sampling and Analysis of Oxidized Inorganic Compounds

by

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INTRODUCTION

With the increasing awareness of the government and scientific communities to the possible hazards from the output of various industries, the Environmental Protection Agency has developed an approach to assess the environmental impact of any type of industrial process. This approach consists of a two phase attack. The first phase, Level 1, surveys the site to detect whether or not a given pollutant class is being emitted. Level 1 (1) sampling and analysis methods are designed to obtain emission results accurate to a factor of two to three. A set of criteria is used to prioritize the streams so that those streams which are found to be a problem are identified for further study. This next phase, Level 2, is designed to be specific for a given stream and perhaps for even a given pollutant. Compared to this phased approach, a direct environmental assessment of a site would use comprehensive sampling and analytical methods to determine all pollutants that are present with high accuracy. TRW has studied the two approaches and found that the phased approach (2) is the more cost effective.

This manual describes an approach to utilizing the data from Level 1 analyses to direct the Level 2 analysis program. The Level 2 analysis, because it is focused, will use more accurate and sophisticated techniques to determine elemental concentrations and identify specific compounds. The analysis of inorganic compounds requires the coordinated use of a variety of analytical techniques. Some techniques, such as X-Ray Diffraction (XRD), Transmission Electron Microscopy with Selected area Electron Diffraction (TEM-SAED) and Electron Spectroscopy for Chemical Analysis (ESCA), have the potential for direct compound identification, but only for selected compounds or situations. The identification scheme proposed in this manual consists of:

- Initial Sample Characterization. Elemental and anion composition, sample stability, and bulk morphological structure are determined.
- Bulk Composition Characterization. Oxidation state, X-Ray diffraction information, and functional groups are derived.
- Individual Particle Characterization. Single particle elemental composition, diffraction pattern, and morphology are measured.

The methods were chosen so that as the analyst proceeds, he is applying more and more sophisticated instrumentation. The degree to which each method can be applied will vary considerably with the experience of the analyst and the sample quantity and equipment available. It is recommended that continuing use of any one method be evaluated in light of the information derived. In general, it is far better to use a variety of instruments operated in the most efficient manner rather than a single instrument or technique to the limit of its capabilities.

In the Level 2 inorganic analysis, the goal is to identify Discharge Multimedia Environmental Goals (DMEG) compounds and concentrations.(3). For every element which exceeded its DMEG concentration value, there is a list of DMEG compounds which contain this element. These compounds are used to develop a list of potential compounds present in the stream analyzed. The decision to continue the analysis for DMEG compounds on the list will depend on a variety of factors:

- Number of DMEG compounds identified exceeding DMEG values.
- Interest in identifying the remaining compounds for those elements that exceeded DMEG concentrations.
- Cost/availability of necessary equipment.

The analyst must decide which information is necessary, what method will be applied, and how much more information can be obtained by each further analysis. In many cases some methods can be bypassed because of results from previous tests; e.g., quantitative anion analysis may provide sufficient information, so that Fourier Transform Infrared (FTIR) analysis would be only repetitious. In other cases efforts may direct the analyst to a specific method since it would be best suited to analyze for a given compound. By understanding the information that can be derived from each technique, the analyst will be better able to select the appropriate combination of techniques to determine the compounds present in an environmental sample of interest.

The compounds discussed in this manual are primarily in higher oxidization states. A companion manual ("EPA/IERL-RTP Procedures Manual for Level 2 Sampling") discusses organometallic or reduced inorganic species analysis. Together the two manuals represent a comprehensive approach to

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16. ABSTRACT The report describes Level 2 analysis procedures for identifying oxidized inorganic compounds in environmental samples from energy and industrial processes. The procedures include: (1) initial sample characterization, (2) bulk sample characterization, and (3) invidual particle characterization. The theory, sensitivity, interferences, sample preparation, application, and information derived are described for each procedure. The report is a step in the development of a general methodology for analysis of process samples. It defines the concepts of Level 2 analyses and reviews currently available procedures. It does not define a fixed protocol because the complexity of samples precludes definition of specific procedures without examination or analysis.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Inorganic Compounds	Stationary Sources	07B
Oxidation		
Sampling		14B
Analyzing		

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inorganic analysis, and should be considered evolving documents to be updated as new technologies are developed.

This manual is organized into four sections. The initial section describes DMEG compounds and their DMEG values and shows how to develop lists of potential compounds based on Level 1 data, DMEG compounds, and potential emissions by process. The next section describes the initial characterization of samples including elemental, anion, thermogravimetric, and morphological studies. This information is used to help interpret X-ray diffraction, IR, and surface studies which are described in the next section. The final chapter describes the use of single particle techniques to characterize particulate matter.

ABSTRACT

This manual describes the Level 2 analysis procedures for the identification of oxidized inorganic compounds in environmental samples from energy and industrial processes. The methods discussed in this manual are grouped into three major phases: 1) Initial Sample Characterization, 2) Bulk Sample Characterization, and 3) Individual Particle Characterization. A description of the theory, sensitivity, interferences, sample preparation, application and information derived is given for each method discussed in the manual. This manual represents a step in the development of a general methodology for analysis of process samples. It is intended to define the concepts of Level 2 analyses and review current procedures available. It does not define a fixed protocol because the complexity of samples precludes a prior definition of specific procedures.

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1.0 EVALUATION AND USE OF LEVEL 1 DATA

The analyst will have the results of the Level 1 survey data for a given site before starting the Level 2 inorganic compound identification work. The Level 1 environmental assessment methodology (1) has been designed to determine inorganic elemental composition of the sampled stream using the combination of Spark Source Mass Spectroscopy (SSMS) and a few wet chemical techniques. The use of this data as the starting point to focus the Level 2 studies will significantly reduce the cost (2) and allow the analyst to select specific methods that are best able to identify the compounds associated with the elements found in the SSMS survey. The following sections will suggest an approach to using the Level 1 data to develop a list of elements for additional study, and will provide information on potential compounds emitted by different processes.

1.1 USING DMEG COMPOUNDS AND DMEG VALUES AS LEVEL 2 TRANSITION CRITERIA

The focusing of the Level 2 analysis effort is achieved by using a yardstick to select streams and elements for Level 2 analysis. The yardstick employed is the Discharge Multimedia Environmental Goals (DMEG) compounds and their concentrations. The DMEG list includes elements and compounds which have been identified in coal and oil treatment processes and are regulated by the EPA or on its lists of pollutants of concern (3).

The DMEG concentrations take into consideration a variety of factors, including toxicity data, half-lives, cumulative tendencies, and relationships between human and animal toxicity data. The toxicity data used to calculate a DMEG value include threshold limit values (TLV); median lethal dose (LD_{50}); median lethal concentrations (LC_{50}); median toxic dose (TD_{50}), and median tolerance limit (TL_m); and carcinogenic, mutagenic and teratogenic data. The DMEG levels are very approximate concentrations and/or contaminants in source emission (air, water or land) that would not result in significant harmful or irreversible responses in exposed humans or ecology when these exposures are limited to short durations (acute effects).

The DMEG list supplies a guide for the Level 2 analyst as it provides a convenient means of organizing a productive approach to inorganic analyses. The inorganic or organic compounds listed in the DMEG charts are not sought by the Level 1 scheme. However, should an inorganic element or organic class exceed a DMEG concentration guideline, then in the phased approach to environmental assessment, a Level 2 assessment would be required to identify and/or quantify the compound forms of the inorganic element of environmental concern.

The DMEG charts, as originally constructed, contain information on the concentration levels of interest. Concentration guidelines are necessary for the decision making process, so that the analyst will know the concentration at which the Level 1 data trigger the Level 2 activities. Comparison of the measured Level 1 concentrations of each inorganic element with the appropriate DMEG decision criterion is used in this manual for proceeding with and directing the more detailed Level 2 studies. Figure 1 depicts the decision logic using the DMEG list at the DMEG concentrations. To illustrate the approach shown in Figure 1, Table 1 lists some inorganic data gathered from a stack sample collected with a SASS train at a power plant. While air data are being used in this example, in other instances the analyst could use the DMEG values for liquids (μg/L) or solids (g/g) depending on the source of the samples.

The analyst will also have a choice of several DMEG values to compare with the actual concentrations found. As a conservative approach, the most toxic compound for a given element is selected and its value used for comparison. The sample concentration is divided by the appropriate DMEG value. If this ratio is greater than 1.0, then that element in the stream deserves further Level 2 attention. Based on the results in Table 1, the elements Li, Be and Pb would be studied further using the Level 2 methodology described in the following chapters.

The DMEG list also provides possible species and compounds (last column Table 1) which might result from oil or coal combustion. Independent of the DMEG compounds, TRW has developed a list of potential compounds by industrial process. This list discussed in the following section should be used to supplement the DMEG compounds to form a comprehensive list of potential compounds emitted from the emission source studied.

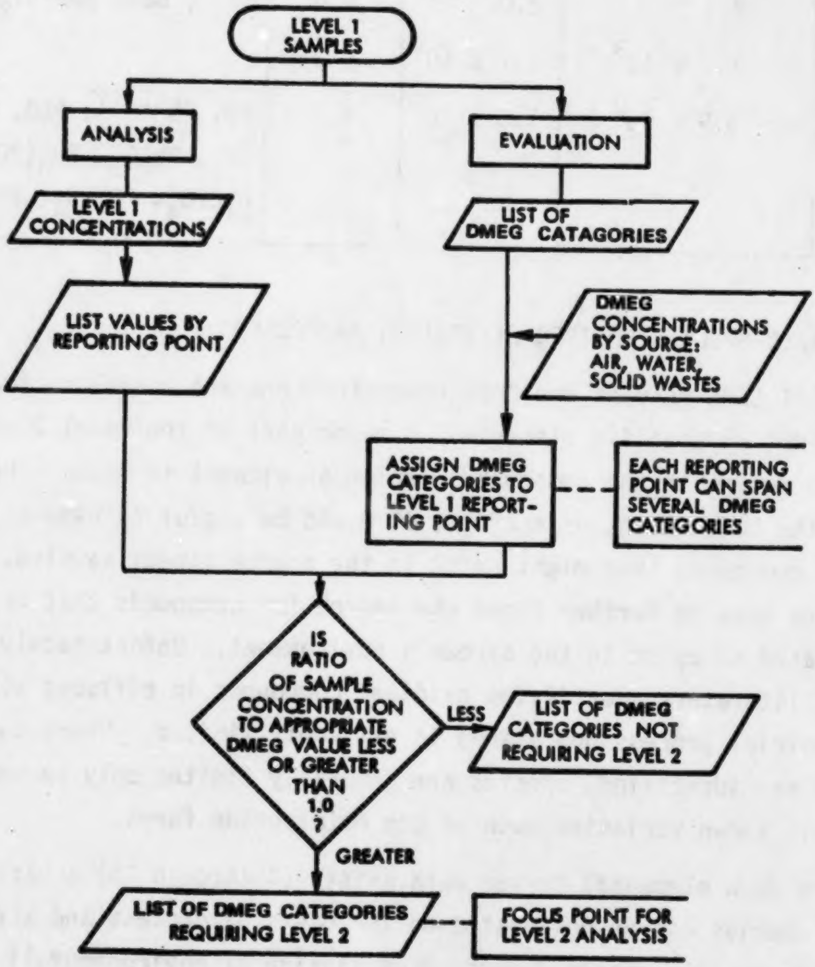
LEVEL 1 SAMPLES
ANALYSIS
EVALUATION
LEVEL 1 CONCENTRATIONS
LIST OF DMEG CATAGORIES
LIST VALUES BY REPORTING POINT
DMEG CONCENTRATIONS BY SOURCE: AIR, WATER, SOLID WASTES
ASSIGN DMEG CATEGORIES TO LEVEL 1 REPORTING POINT
EACH REPORTING POINT CAN SPAN SEVERAL DMEG CATEGORIES
IS RATIO OF SAMPLE CONCENTRATION TO APPROPRIATE DMEG VALUE LESS OR GREATER THAN 1.0 ?
LESS
LIST OF DMEG CATEGORIES NOT REQUIRING LEVEL 2
GREATER
LIST OF DMEG CATEGORIES REQUIRING LEVEL 2
FOCUS POINT FOR LEVEL 2 ANALYSIS

Figure 1. Decision Procedure for Level 1 to Level 2 Transition

Table 1. Application of DMEG Decision Criteria

Compound Category	Measured Level 1 Source Concentration ($\mu g/m^3$)	DMEG ($\mu g/m^3$)	Sample/ DMEG ($\mu g/m^3$)	DMEG Compounds Sought in Directed Level 2 Analysis
Li	2.3×10^2	2.2×10^1	10.5	Li^+, LiF, Li_2CO_3, and LiH
Be	4.1	2.0	2.0	Be^{++}, BeO, $BeO \cdot Al_2O_3 \cdot SiO_2$
B	1.0×10^3	3.1×10^3	0.3	
Pb	9.5×10^2	1.5×10^2	6.3	Pb, $Pb^{+2,+4}$, PbO, $PbSO_4$ PbS, $PbCO_3$, $Pb_3(PO_4)_2$, $PbCrO_4$, $PbMoO_4$, $PbHAsO_4$

1.2 OXIDIZED SPECIES EMITTED BY VARIOUS PROCESSES

Level 1 SSMS results and DMEG concentrations are useful to focus additional effort on specific elements. A major part of the Level 2 effort will be to determine the compound in which an element is bound. Prior to starting the Level 2 analysis effort it would be useful to have a list of potential compounds that might exist in the source stream sampled. This list can be used to further focus the search for compounds that are known or postulated to exist in the stream's environment. Unfortunately, the amount of literature identifying oxidized compounds in effluent streams from industrial process operations is extremely limited. Where such effluents are identified, species are generally limited only to commonplace, well known varieties such as the metal oxide forms.

Where such elemental survey data exists (4 through 15) a variety of oxidized species can be postulated on the basis of process and stream reaction chemistry. Table 2 presents a listing of environmentally significant elements found to exist in effluent streams from various process technologies. In each case, oxidizing agents exist either as a stream constituent, a process reactant, or both. Table 3 presents a selected listing of some of the more well known technologies along with typical effluent characteristics common to each process type. Information from both Tables 2 and 3 was used to postulate the probable existence of various

Table 2. Elemental Effluents Cited from the Literature

Industry Type	O	Sb	As	B	Ba	Be	Cd	Cr	Cu	Mn	Mo	Pb	Se	Sn	V	Zn	Hg	Ni	d	F	S
Electroplating								X										X			
Copper Smelting (Primary)	X	X	X				X		X			X	X				X				X
• Roasting	X		X				X		X			X	X								X
• Reverberating	X		X				X		X			X	X								X
• Converters	X		X				X		X			X	X								X
Zn Smelting (Primary)	X		X				X					X	X			X	X				
• Roasting	X		X				X					X	X			X					
• Sintering	X						X					X				X					
• Distillation	X						X					X				X					
Copper Smelting (Secondary)	X	X					X		X			X	X			X					
• Sweating Furnace	X						X		X			X				X					
• Blast Furnace	X								X			X				X					
Coal Fired Boilers	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Oil Fired boilers	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Sewage Sludge Incineration	X			X			X			X							X				
Grey Iron Foundry	X		X		X	X	X		X	X		X		X	X			X		X	X
• Cupola	X		X			X				X		X		X	X			X		X	X
Glass Manufacture	X	X		X	X								X								
Paper Pulp Industry	X	X						X									X		X		X
Ceramic Industray	X	X		X		X									X						
Municipal Incineration	X						X						X		X	X	X				
Lead Smelting (Primary)	X	X	X				X					X	X				X				X
• Sintering	X	X	X				X					X	X								X
• Blast Furnace	X		X				X					X	X								X
• Reverberatory Furnace	X		X				X					X									X
Pesticide, Herbicide, Manuf.	X		X	X			X										X		X	X	
Petroleum Refineries	X	X	X			X	X	X		X		X	X		X		X	X	X		X
Coking Operations	X	X	X			X	X	X		X		X	X		X		X	X	X	X	X
Nonferrous Alloys Furnaces	X						X											X			
Steel Manufacture	X				X		X	X	X	X	X	X		X	X	X		X		X	X
• Blast Furnace	X				X				X	X	X	X			X	X		X		X	X
• Open Hearth Furnace	X				X				X	X	X	X		X	X	X				X	X
• Basic Oxygen Furnace	X				X				X	X	X	X			X	X				X	X
• Electric Arc Furnace	X				X				X	X	X	X				X				X	X
Cement Manufacture	X														X			X			
Aluminum Smelting	X		X		X	X				X	X				X			X	X	X	X

Table 3. Conditions and Typical Inorganic Compounds Emitted from Various Industrial Processes

	Effluent Characteristics from Predominant Process Operations					Oxidized Species Present in Primary Effluents	
	Particulate Data						
Process Identification	Size Distribution	gr/SCF	Flow Rate (1)	Temperature °F	Moisture Vol %	Cited from Literature	Probable Based on Stream Chemistry
1) Steel Plant						G, L, S Fe_2O_3, FeO, Cr_2O_3 SiO_2, Al_2O_3, CaO, MgO, MnO, ZnO, CuO, NiO, PbO, F, Ba, Cd, Mo, Sn, V, SO_2, SO_3	G The fluoride and sulfide forms are possible for all these metals. L All indicated forms also probably exist in liquid effluent streams.
(a) Blast Furnace	15-90% <74μ	4-30, 7-10 avg	(a) 40-140 (b) 60-138	390 at throat 3000 at furnace	9.6		
(b) Sinter Plant	15-45% <40μ	0.2-3.2	(a) 30-460	100-400	2-10		
(1) Windbox:	9-30% <20μ 4-19% <10μ 1-10% <5μ		(b) 148-230				
(2) Discharge end:	80% <100 10 <10	1-5	(a) 0.03-0.2	100-300	-		
(b) Coke Ovens						G HgO, SeO_2 L As_2O_3, V_2O_s	G Oxides and sulfides and halogenated species are probable for the following elements (see Table 1): Sb, A_s, Be, Cd, Cr, Mn, Pb, Se, V, Hg, Ni L The Quench water will contain all of the above as well as oxidized forms of most of the trace elements found in coal.
(1) Oven off gas	Highly variable	1-15	2.1 M ft^3 per charge	≤1832	Variable depending on point in coking cycle		
(2) Quench Tower	95-97% >47μ	0.05-0.1	900 M ft^3 per quench	140-150	Effluent consists primarily of steam		
(3) Sour Quench Water	Not applicable	-	Water usually sluiced; flow variable and cyclic	-	-		
2) Coal Fired Boilers	25% <10 49% <20 79% <44	2.9 to 3.7 avg	(a) 297-397 (b) 362-434	245-258	6.4	G, L, S SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, Ni_2O, TiO_2, K_2O, FeO, P_2O_5, SO_3, SO_2, NO_x, O_2 (6.2 to 6.8%), chlorides	Oxides, sulfides and halogenated species are probable for the following elements: Sb, As, B, Ba, Be, Cd, Cr, Cu, Mn, Mo, Pb, Se, Sn, V, Zn, Hg, Ni. Ash and aqueous effluents also contain all species listed.

(1) Flow rate is expressed in: (a) M SCFM or (b) M SCF/ton of product processed.
G = gaseous phase; L = liquid phase; S = solid phase.

Table 3. Conditions and Typical Inorganic Compounds Emitted from Various Industrial Processes (Continued)

Process Identification	Effluent Characteristics from Predominant Process Operations					Oxidized Species Present in Primary Effluents	
	Particulate Data						
	Size Distribution	gr/SCF	Flow Rate	Temperature °F	Moisture Vol %	Cited from Literature	Probable Based on Stream Chemistry
Forest Products Industry						G, L, S CO_2, O_2, SO_2	G, L, S Chlorides, hypochlorites, and oxides are highly probable for a wide variety of elements due to bleaching and other oxidizing operations.
(a) Kraft Pulp Mills							
(1) Recovery Furnace	50-85% <2μ	3-8 avg 3.8	(a) 20-568 (b) 278-568	270-650 avg 350	20-40	Sb, Cr, Zn,	
(2) Lime Kiln	95% <25μ	3-20	(a) 7-50	400-900	400-600 lbs/air dried ton	Carbonates, sulfates, chlorides and oxides are cited in the literature as general groups.	
(3) Smelt Dissolving	90% <5μ	0.17-1.3	45 SCF/air dried ton	170-200	670 lbs/air dried ton		
Primary Nonferrous Metals Industries							
(a) Copper						G, L	
(1) Roasting Furnace	15% <10μ	6-24	(a) 60-131	600-890	-	As_2O_3, Sb_2O_3, Al_2O_3, SiO_2, SO_2, SO_3, Cd, Pb, Se, Hg, O	Cd, Pb, Se, and Hg oxides, sulfites, and sulfates are probable.
(2) Electrolytic Refining*							
(b) Lead						G, L	
(1) Sinter Machine	100% <10μ	0.4-4.5	(a) 140 (b) 130	250-600	-	As_2O_3, CdO, $CdSO_3$, $CdSO_4$, CdSe, TeO, PbO, Pb_3O_4, ZnO, Sb, As, Mo, Hg, O	Compounds of varying oxidation states are probable, i.e.: TeO_2, TeO_3, $(TeO_2)_2SO_3$ etc. Also CdTe and other complexes.
(2) Blast Furnace	0.03 to 0.3	1-11	6-14	150-250			
(c) Zinc							
(1) Roaster	14% <5, 31% <10, 70% <20	5-65	25-30	730-900	-	As, Cd, Pb, Se, Zn, Hg (from Table 1), O	Oxidized species in varying oxidation states are probable in gaseous and liquid effluents
(2) Sinter Machine	100% <10	0.4-4.5	140	320-700	Dew Point: 122-140		
(d) Aluminum	Submicron particulate		2000 to 4000 CFM/cell	-	-	G	
(1) Reduction Cell		0.03-2.0				Al_2O_3, SiO_2, Fe_2O_3, Na_2O, Fluorides, O	Significant quantities of the following have been found as a result of T-4 field effort: Be, chlorides, V, Mo, Se, S, bromides, As, Ni, Ba, Mn. These elements may exist as halides, oxides, or in various sulfur forms.

*Process data for electrolytic refining is highly variable; literature does not cite specific flow data.

Table 3. Conditions and Typical Inorganic Compounds Emitted from Various Industrial Processes (Continued)

	Effluent Characteristics from Predominant Process Operations					Oxidized Species Present in Primary Effluents	
	Particulate Data						
Process Identification	Size Distribution	gr/SCF	Flow Rate	Temperature °F	Moisture Vol %	Cited from Literature	Probable Based on Stream Chemistry
Refinery Operations (a) Claus Plant (oil/gas) (b) Fixed Bed Catalyst Regeneration (c) Moving Bed Catalyst Regeneration (d) Fluid Coker off-gas				Fixed and moving bed regenerable catalyst function at about 850 to 1000°F at 300 to 700 psig		Bromides, chlorides, fluorides, SO_2, SO_3, Al, Ba, Be, Br, Ca, Cd, d_0, Fe, K, Li, Mg, Na, Ni	A wide variety of oxide sulfur form and halogenated species are possible for all environmentally significant elements. While specific compounds are not cited in great detail in the literature, many analyses identifying the existence of classes are available, i.e., halides sulfur forms, oxides etc. All may be in G, L, and S forms.
Coal Conversion[1] (a) Gasification and Liquefaction Operations (1) Coal Preparation (2) Quenching and Cooling (3) Fixed Bed Catalyst Regeneration: (4) Sulfur Plant: (5) Tar Separation	Same parameters and species as defined under "Refinery Operations."					All elements associated with coal are found in G, L, and S coal conversion effluent streams.	Gasifiers are oxygen or air blown, stream chemistry is complex, physical conditions are extreme. Process conditions are ideal for the formation of a wide variety of oxidized species in both gasification and liquefaction systems.
Fertilizer Manufacture	6.3% <5μ, 12% <10μ 22% <20μ 29% <30μ 34% <40μ	0.7 to 4.0	(a) 16.5 (one unit)	201	-	G, L, S P_2O_5, SiO_2, Al_2O_3, MgO, CaO, Fe_2O_3, fluorides, O_2, SO_2, SiF_4, HF	A number of trace elements, in addition to those listed, exist in G, L, S effluents. Stream chemistry is conducive to the formation of oxides and fluorides.

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[1] Stream parameters are highly variable depending on process design, see text.

Table 3. Conditions and Typical Inorganic Compounds Emitted from Various Industrial Processes (Continued)

Process Identification	Effluent Characteristics from Predominant Process Operations					Oxidized Species Present in Primary Effluents	
	Particulate Data						
	Size Distribution	gr/SCF	Flow Rate	Temperature °F	Moisture Vol %	Cited from Literature	Probable Based on Stream Chemistry
Oil Fired Boilers	90% <1μ	0.013 to 0.2, avg: 0.05.	Horizontally fired: 348 to 780	315	8.4	G O_2 (0.7 to 13.2%), SO_2, SO_3, NO_x, chlorides, Fe_2O_3, CrO_2, NiO, V_2O_3, Co_2O_3, SiO_2, Al_2O_3, BaO, MgO, PbO, CaO, Na_2O, CuO, TiO_2, MoO_2, B_2O_3, MnO_2, SrO, TiO	Other significant trace elements found in oil particulates include: Sb, As, Be, Cd, Se, Sn, Zn, Hg. These elements also probably exist as oxides. All elements listed may exist as chlorides and in various sulfur forms.
		0.13 to 0.19 during soot blowing	Tangentially fired: 384 to 396	270			

oxidized species in process effluent streams for the technologies listed. The existence of such species may be predicted with a high confidence level because ionization energies and heat of formation energies of numerous compounds are well within process operating conditions. Also, the existence of even a few literature-cited oxidized species is enough to indicate the existence of generic compound types where elements with similar reactivities have been found.

The assumptions used to postulate the existence of oxidized species (far right-hand column - Table 3), other than those cited in the literature, are as follows:

- The existence of oxidizing agents present either in the stream or during process operations or both.
- The existence of literature-cited oxidized species within the process stream.
- The existence of temperature and pressure conditions equal to or above ionization and/or heat of compound formation for literature-cited elements.
- The composition of feed material and process reactants.
- The elemental analysis of acquired samples such as SSMS (such as the presence of Cl or F in a solid particulate sample indicating the presence of chlorides or fluorides).

The data provided by Table 3 should be used in two ways. In most cases the list of DMEG compounds given for a specific element will include compounds not present in effluent from the process being studied. Using Table 3 those compounds can be removed from the potential compound list to be studied and/or added to by other compounds not listed in the MEG categories. In addition to this use Table 3 provides information on the mass loading, which can be used to specify sampling times to obtain enough sample for later Level 2 chemical analysis. The following section will provide some guidelines for Level 2 sampling.

1.3 LEVEL 2 SAMPLING

No matter how accurate or precise the analysis procedure, the validity of the results depends on the accuracy of the sampling procedure. Current

Level 1 sampling procedures for liquid and solid samples are probably sufficient for most Level 2 efforts with the provision that:

- Samples are time-integrated to account for process operational variances.
- Specialized sampling procedures are employed for unstable species.

The following techniques or procedures have been selected to provide an overview and guidance for the selection of an appropriate Level 2 sampling method.

1.3.1 Solid Sampling

Solid Sampling covers a broad spectrum of material sizes ranging from large lumps to powders and dusts. There is an equally diverse assortment of potential sample sites including railroad cars, large heaps, plant hoppers, conveyor belts, and process stream pipes. Obviously no one method or piece of equipment is suitable for all situations, but the advantages and disadvantages of each must be weighed in the light of individual field test conditions. The following discussion provides an overview of common solid sampling situations and summarizes the sampling approaches and alternatives available to a field test team.

1.3.1.1 Sampling Methodology and Equipment Survey

The Level 2 sampling of solids may include the use of three manual grab sampling techniques: shovel sampling; boring techniques, which include pipe or thief sampling; and auger sampling. Mechanical samplers, both moving and stationary, can also be used to obtain solid samples. The chief consideration of solid sampling is the acquiring of representative samples.

Shovel sampling procedures include grab sampling, coning and quartering, and fractional shoveling. Grab sampling consists of taking small, equal portions at random or regular intervals, typically from railroad cars, large heaps, or hoppers. The method is quick and inexpensive. However, grab sampling makes no allowance for segregation of the sample by particle size and also tends to give consistently high or consistently low results depending on the person sampling. As such, grab sampling should be used for survey sampling.

Coning and quartering consists of carefully piling the material into a conical heap, with subsequent flattening of the cone into a circular cake. The cake is then marked into quadrants; two opposite quadrants are taken as the sample and the other two quadrants are discarded. The entire process is repeated until the desired sample size is obtained. In general, this method is time-consuming and the symmetry of the intended vertical size segregation is difficult to achieve in practice.

Fractional shoveling is applicable to materials being loaded, unloaded, or moved from one place to another by shoveling. In fractional shoveling, every third, fourth, fifth, or tenth shovelful is taken as the sample. This method is inexpensive and relatively fast. If performed conscientiously, fractional shoveling can be more reliable than coning and quartering. However, its applicability is limited and errors are easily introduced by carelessness.

Pipe boring techniques represent another class of solid sampling methodology applicable to material stored in piles, silos or bins. The usual method of pipe boring is to insert the pipe into the material to be sampled at regular intervals. The method is fairly reliable provided that the pipe is long enough to reach the bottom of the material. However, it is only applicable to fine or powdered dry materials, because lumps or any stickiness will jam or plug the pipe. Small pipe borers can be used to sample sacks or cans of material. There are primarily two designs of pipe borers that give best results. One is a simple pipe that is tapered so the end first inserted is smaller in diameter than the handle end. A more sophisticated design, known as a thief, makes the sample more representative vertically. It consists of two close-fitting concentric pipes sealed at the base in a conical point. Longitudinal slots are cut along the side of each pipe. The thief is inserted with the slots turned away from each other and then, when the sampler is in position, the outer pipe is rotated, lining up the slots and allowing the inner pipe to fill the sample. For proper results with any design of pipe borer, the opening through which the sample material passes (slots or circular pipe ends) must be large relative to the maximum particle size.

Auger samplers, a form of drill, pack the sample in the helical groove of the auger and can be enclosed in a casing if the nature of the sample is such that it will spill when the auger is removed from the hole. Like the pipe borers, they are simple to use and have the further advantage of being applicable to a greater variety of materials. For example, augers work well for materials that are packed too hard for a pipe sampler to be forced in. For very packed materials, machine-driven augers are available. However, a thief sampler would be the better choice if sample spillage is a possibility. Also, both pipe samplers and augers yield poor results if the material being sampled is poorly mixed.

Mechanical samplers require that the sample material be in motion to present it to the cutters as a thin ribbon or stream. Design considerations for feeding these samplers and catching the sample and rejected material generally necessitate the permanent installation of the sampler into the flowing sample stream. Numerous mechanical samplers have been designed; the most popular designs have been variously modified to satisfy specific applications. However, all mechanical samplers fall into two general types: those that take part of the stream all of the time (stationary samplers), and those that take all of the stream part of the time (moving samplers).

In stationary mechanical samplers, the entire sample stream is fed continuously through the device and stationary cutting edges divide out and remove specific fractions. The two best-known designs of this type are rifflers and whistle-pipes.

Rifflers take several slices of the stream by means of parallel chutes alternately placed at 90° angles to each other, thereby cutting the stream in half. Successive rifflers can be arranged in banks to cut the stream into any desired fraction. The smaller the chute width, the greater the number of increments in the sample. Therefore, the accuracy of riffler sampling increases as the ratio of chute width to particle size decreases, to the limiting condition where the chutes tend to clog. In general, chutes should be at least three times the diameter of the largest size particle to avoid clogging. Care must be taken to feed the riffler with a well-mixed, uniform sheet of material since any compositional variations due to cross-sectional segregation are multiplied by a bank of rifflers.

A whistle-pipe sampler consists of a vertical pipe with notched openings cut halfway through the pipe, each spaced 90° horizontally from the one above. Rectangular steel plates are placed in the notches at a 45° angle to the vertical so that the top edges coincide with a diameter of the pipe. Thus each notch halves the sample and, with a series of five openings, the sample obtained is 1/32 of the original volume. The same fraction with improved accuracy can be obtained by using a cutter arrangement that quarters the stream, rejecting opposite quarters, and spaces each cutter at 45° horizontally from the one above. In either design, a hopper-shaped liner is placed above each notch to re-center the stream before it reaches the next cutter.

Both rifflers and whistle pipes have irresolvable design problems that reduce their reliability. Worn or bent cutting edges distort both the volume and the particle size distribution of the sample. The housing necessary for these samplers prevents examining them for clogged openings while in operation. Material streams whose composition varies along the transverse section are even further segregated by either of these samplers.

Moving samplers consist of cutters that move through the free-falling sample stream taking all the stream for the duration of time they are moving through it. There are two ways of effecting this. One is with rotating or oscillating samplers whose cutters are set on the radii of an arc, and the other is with straight-line samplers whose cutting edges are set parallel to each other and perpendicular to the line of their path.

Among the well-known designs of rotating arc-path samplers are Vezins, Synders, and Chas. Synders. They all consist generally of scoops with vertical sides, set on an axis parallel to the stream flow. The best oscillating samplers are known as Bruntons. The scoop travels back and forth across the stream in a pendulum-type motion. The travel path must be sufficiently long to minimize the bias created by taking more samples from the sides of the stream than from the middle. All the arc-path samplers have the advantage over stationary samplers in that they take an accurate cut, are simply constructed, and are accessible for observation while in operation. However, damp sample material may tend to clog the scoops and care must be taken to maintain the cutting edges in good condition and to keep them completely radial.

The straight-line samplers are generally considered to be the most reliable and accurate of all available types of samplers. The design of their cutters is such that the sampling scoop spends an equal amount of time in every portion of the stream. Generally the travel is at right angles to the stream. Though they provide increased reliability, these samplers require more maintenance and attention because of their increased mechanical complexity.

1.3.1.2 Sample Collection and Storage

It is always preferable to sample a moving stream either in pipes or from conveyor belts, particularly if there is a large particle size range in the material. Stored containers or heaped beds of material tend to settle, creating segregation of particles according to size and density, and it is difficult to compensate for this bias in the sampling. Furthermore, large masses of stored material are extremely difficult to handle. The interior portions are relatively inaccessible and the amount of time and space needed to move the material enough to take a representative sample can quickly become prohibitive. However, such situations can generally be avoided by a good sampling test plan.

Typically, the solid materials of interest are the feed materials and the residues from particulate scrubbers such as baghouses, high energy venturis, and electrostatic precipitators. Raw feed stock as it passes through the process stream may pick up other materials as contaminants and, therefore, differ greatly in composition from what is finally being fed to the process. Consequently, samples should be taken at the last possible site before the stream is fed into the process. This means that sampling will generally be conducted from a feed hopper, if accessible, or from whatever pipes or conveyors feed the material to the process. Similarly, scrubber residues can be sampled from whatever collection hopper the device has or from pipes going to the hopper. Extra handling steps only increase the chances of the sample becoming contaminated.

As part of their own process control, many plants may have some type of mechanical sampler already installed into their process stream. Whenever possible, these devices should be used for taking samples. They are reliable, take representative samples, and are fast and easy to use. Before being used, however, the samplers' operation and cutting edges should be checked to ensure accuracy. If reliable automatic samplers are an integrated part of the plant and are available, no sampling equipment will be needed by the field test personnel.

In cases where it is decided to take samples from moving conveyor belts, the standard procedure is to stop the conveyor at regular intervals (e.g., every 10 to 15 minutes) and shovel off a section of the material. This is continued until the desired sample size is obtained. Flat-nosed shovels with straight perpendicular sides are best for these sampling purposes.

Another alternative is to sample process streams as they move through pipes if there are appropriate ports. A variety of pipe samplers are commercially available. The type most suitable for trace element sampling is the pneumatic sampler, which eliminates the screw type or scraping action of other types of samplers which grind the sample and abrade the sampler, thereby introducing considerable contamination.

An example of a pneumatic sampler is the Model RTA of Quality Control Equipment Corporation. All parts in contact with the sample can be Teflon or nylon lined, which is a major advantage. It can be used to sample solids with a particle size less than 0.64 cm (1/4 in. in diameter), as well as slurries and liquids from pipes fitted with at least 2-inch diameter sampling ports. Samples collected by any of the techniques described must be stored in pre-washed and dried plastic bottles or plastic lined drums. If plant personnel are to take the sample, they should be provided with the appropriate bottles or containers.

1.3.2 Liquid Sampling

The factors which must be considered in accurately sampling a fluid stream for inorganic materials include:

- Stream homogeneity
- Stream flow rate and variations
- Prevention of sample loss
- Sources of contamination
- Sample size.

Of these, stream homogeneity is perhaps the most important factor. Unlike stack effluent streams which are mixed fairly evenly due to higher thermal agitation and lower fluid viscosities, liquid streams tend to be more stratified and require more careful sampling. A flow-proportional, composite sampling technique is required for sampling liquid and slurry streams for trace materials. By comparison, obtaining a composite representative gaseous sample from a stack, a traverse of the pipe or duct is made. However, this is usually impractical in sampling liquid streams.

In liquid streams, a composite sample can be taken by using several differently positioned probes, a single multiported probe, or a combination of these. While either of these approaches is suitable, the single multiported sampler is usually more convenient.

In the case of slurry sampling, it is also important to avoid segregation of liquid and solid phases. This is similar to the requirement for isokinetic sampling in particulate-laden gas streams. An EPA internal study evaluated 60 commercially available models of automatic sewer flow samples (126). In this study, sampling velocity was determined to be the most critical factor in sampling sewage slurries. Two units were found to perform acceptably: Quality Control Equipment Company Model CVE and Testing Machines, Inc. Fluid Stream Sampler. Both of these units are portable and completely automated. The QCEC unit also has a built-in ice chamber for automatic refrigeration of temperature-sensitive samples. Another common practice for the preservation of liquid samples is to freeze them until they are ready for analysis. However, this practice is now being questioned for trace material analysis because of the tendency for metal ions to precipitate upon freezing. The technique should only, therefore, be used for preserving samples for bacteriological analyses.

It is well known that trace materials in liquid phases may be lost from a sample through adsorption on sampling line or reservoir surfaces. Borosilicate glass (Pyrex) surfaces appear to be particularly effective in removing trace heavy metals, especially under alkaline conditions. However, plastics such as polyethylene, polypropylene, and Teflon show little or no tendency to adsorb inorganic materials.

In addition to sample loss due to surface adsorption, a sample may also be contaminated by elements from those surfaces. Surface wall material can be deposited in a sample either by a chemical extraction of the wall materials by agents in the sample or by physical abrasion or erosion of the wall by a sample. The latter case could be a significant problem for slurry systems because the abrasive nature of the sample could expose unpassivated layers of the wall to chemical interaction with the sample.

Another important factor which must be considered in sampling liquid streams for inorganic material constituents is the sample size requirement. Two principal requirements govern sample size. The first requirement is that the amount of sample collected must be sufficient for the testing and analysis procedures to furnish accurate and precise results. The second requirement is based on the statistical sampling error that can be tolerated. The minimum sample required for analysis varies between 1 and 1000 μg for the trace materials of interest using the proposed analysis procedures. For the lower ppm concentration levels of interest, this translates into minimum sample volumes ranging between one ml and one liter. This range of sample volumes is easily within the operating limits of presently available liquid sampling equipment and presents no special difficulties.

1.3.2.1 Equipment

The sampling of liquids and slurries in the categories defined above requires equipment suitable for point sampling, as well as for sampling from ponds, reservoirs, open tanks, open channel flows, and pipes which have built-in sampling ports.

For pond and tank sampling, and in preliminary or point sampling, point and depth-integrated samplers are commonly used. The Sirco Uniscoop, which is made of No. 316 stainless steel, is recommended for point sampling. The Uniscoop has a handle for collecting below-surface samples and is convenient to use. A depth-integrated sampler consists of a weighted bottle and is easily fabricated.

The recommended automatic samplers are Model CVE (Quality Control Equipment Corporation) and Model 1940 (Instruments Specialty Corporation). All components in both units which come in contact with the sample are composed of polypropylene, polyethylene, or Tygon, and the sample never passes through any valves or pumps. Both units can perform short-term or long-term sampling at certain time intervals proportional to time or flow rate. The units also have built-in ice cabinets to preserve the samples at lower temperatures. The units offer a long-term stability without mechanical or electronic malfunctions.

While the Model CVE sampler provides composite samples directly in the field, and the Model 1940 takes sequential samples that are stored in separate bottles, both models can perform time or flow proportional sampling depending on the availability of a flow measuring device. The Model CVE was rated the best unit in a study conducted by the EPA Regional Office at Kansas City, Missouri.

The equipment discussed in this chapter is capable of handling a wide variety of process streams found in most industrial applications. For sampling streams having highly corrosive materials, the Teflon coating of all metal parts should be considered in order to prevent contamination of the samples and corrosion of the sampling equipment. However, for most applications, inherent durability and flexibility of the off-the-shelf samplers are adequate.

1.3.2.2 Sample Collection Separation and Storage

Prior to sample collection, the liquid sampler must be cleaned in the field to prevent any contamination. The sampler is flushed out with a liter (quart) of nitric acid (1:1) followed by several liters of high purity water to eliminate any particles introduced during shipping and field storage. The sampler is then placed near the process stream to be sampled. This site should be free of windblown contamination. The sample probe or hose is introduced into the stream and the timer set for the proper sampling period.

All storage bottles that are going to be in contact with liquids must be cleaned to prevent contamination of the sample by elements leaching from the container material. The following procedure (127) is recommended for most plastic bottles:

1. Fill with 1 + 1 HCl (AR grade).
2. Allow to stand one week at room temperature (80°C for Teflon).
3. Empty and rinse, with distilled water.
4. Fill with 1 + 1 HNO_3 (AR grade).
5. Allow to stand one week at room temperature (80° for Teflon).
6. Empty and rinse with distilled water.
7. Fill with purest available distilled water.
8. Allow to stand several weeks or until needed, changing water periodically to ensure continued cleaning.
9. Rinse with purest water and allow to dry in a particle- and fume-free environment.

Following sample collection, the various phases present in a liquid or slurry must be separated to prevent either gross disruption of the material content of each phase or the oxidation of selected species due to continued contact with the liquid phase. For these reasons a preliminary field phase separation procedure is recommended for all slurry streams.

The equipment necessary for separating the phases of a slurry sample in the field consists of:

- Filters (Gelman Acupore 1.2 μm)
- Nalgene Buchner funnel and filter flask
- Small vacuum pump
- Acids, bases, 50% Acetone solution, and high purity distilled water.

All the Nalgene equipment used in separation of the sample phases should be pre-washed using the procedure presented above to prevent contamination. A solution of 0.1 N HNO_3 (high purity) in a squeeze bottle must be used as a rinse between samples to prevent cross-contamination. Enough clean replacements should be available, in the event that the liquids leave a film on the plasticware.

Stabilization Procedures

For most cases, the standard EPA preservation procedures (128) can be used to stabilize the liquid samples obtained. The procedures include the two basic approaches for cations and anions. In both cases the liquid position of a sample is divided in half and placed in the pre-cleaned plastic storage bottles. Into one container enough HNO_3 (High Purity) is added to reduce the $pH < 2$. This amount is recorded as well as the original volume of liquid stabilized. The addition of HNO_3 stabilizes the trace metals and prevents absorption on the container walls. With the exception of Hg, these samples are stable up to 6 months. It is recommended that Hg be stored no longer than 13 days in plastic containers due to its ability to permeate the plastic container and the possibility of Hg diffusion from the laboratory air into the container.

Stabilization of anionic species is slightly different. Most anions can be stored in the plastic container at 4°C, but only for a limited period of time. Chloride, F^-, and $SO_4^=$ can be stored up to 7 days, while Br, I^-, NO_3, should be analyzed within 24 hours of collection. Reference 128 provides more detail on these and other anions.

For water-solid streams, the slurry is first filtered using equipment and filters described above. The filtrate is stabilized like the clear liquids. The filtered solids are rinsed with a 50% acetone solution to remove excess moisture, while minimizing dissolution of the solids. This procedure works very well with Flue Gas Desulfurization (FGD) sludges, and is applicable to solids obtained from oxidizing processes. The rinsed filter cake is then dired in an oven (explosion proof) at 110°C.

1.3.3 Gas Sampling

Level 2 gas sampling is divided into three separate categories:

- Fugitive Gas Emission
- Flue Gas Emission
- Flue Gas Particulate Emissions

The following sections will present some guidelines for Level 2 sampling methodologies for these categories.

1.3.3.1 Fugitive Gas Emissions

Sampling particulate matter from fugitive emissions requires a well thought-out strategy. IERL/RTP has specified a variety of procedures in Reference 17.

1.3.3.2 Flue Gas Emissions

It is recommended that all gas samples be time integrated to improve the overall accuracy of the analysis. Most oxidized species can be sampled with either polymeric (e.g., TEDLAR), or glass containers. The best approach is to use on-line continuous monitors whenever possible. Continuous readout will provide valuable information on the cycles or changes in the emission as the process varies.

1.3.3.3 Flue Gas Particulate Emissions

After the Level 1 analysis has been completed on the particulate samples taken from the SASS train, the analyst must decide whether to initiate the Level 2 analysis on the remaining SASS train samples. The use of samples from a SASS train are attractive from the cost and time standpoint. There are other points which should be considered prior to initiating the Level 2 analysis program on SASS train samples:

- Single point. While every effort is made to pick a representative point, flow fluctuations and particle stratification can lead to sampling errors on the order of a factor of 2 at stack or control device inlets and as high as a factor of 3 at the outlet of control devices.
- Contamination of Samples. The SASS train is an all SS 316 train which means there is a definite potential for Ni, Cr and Fe contamination. Nickel, Cr, and Fe contamination is especially prevalent in gas streams containing SO_2 and HCl. The main point of attack is in the condensor module where dilute solutions of H_2SO_4 and HCl will readily attack the condensor surface. Because of these problems, it is recommended that an alternate, all glass train (Figure 2) be used for Level 2 testing. This train has been used in field tests and because of its all-glass design Ni, Cr, and Fe can be monitored. The train itself consists of a particulate section which has a 3 μ cutoff cyclone and a glass fiber filter. The particulate section is followed by a series of oxidative impingers which use the same chemistry as the SASS train. The main drawback with these glass trains is that they currently are designed to sample at 28 Lpm (1 cfm). This low sampling rate is partially offset by the high sensitivity of most inorganic analytical techniques and by its ability to perform a complete traverse of the flue gas stream.

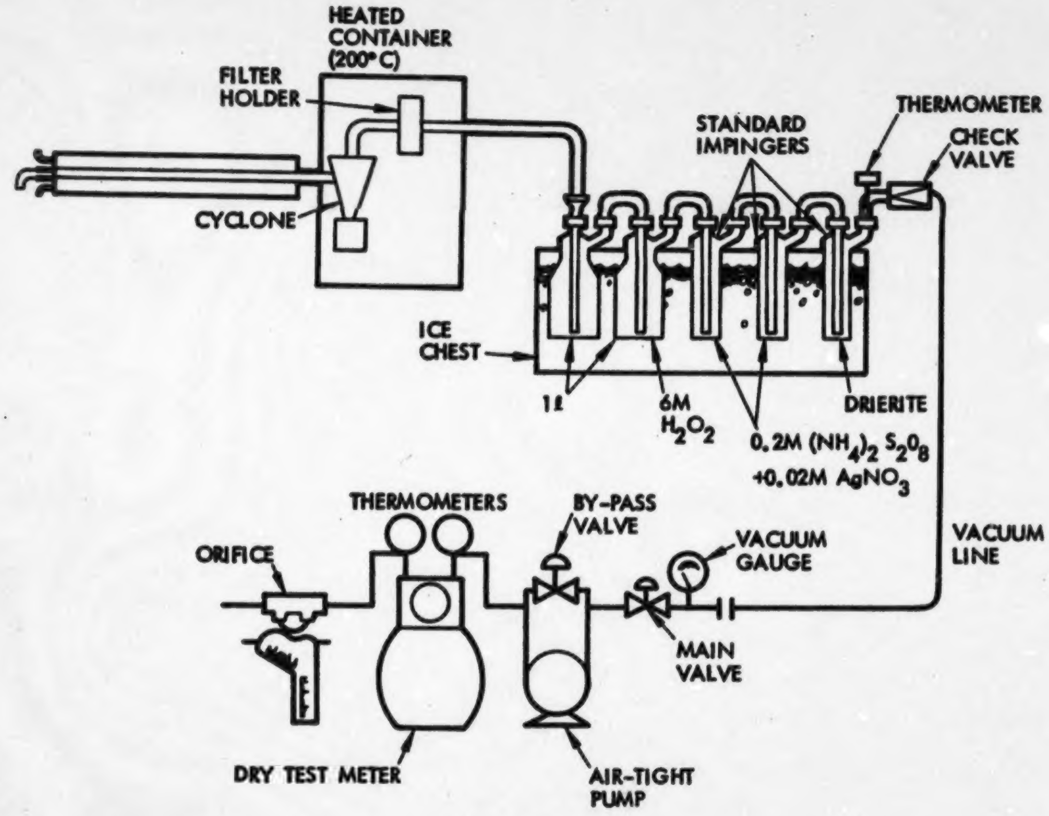

Figure 2. Level 2 Inorganic Sampling Train (Glass)

In addition to obtaining a bulk sample, particle size impactors can be used to provide sized particle samples for analysis. Section 2.5.3.2 describes the use of an impactor to perform elemental analysis by particle size.

2. INITIAL SAMPLE CHARACTERIZATION

In the first phase of the sample analysis, the goal is to determine accurately the elemental and anion composition of the sample as well as its general physical and morphological characteristics. The techniques used to perform this characterization are summarized in Table 4. Developing a list of potential compounds has already been discussed in Section 1. The next step is to view the sample under a Polarized Light Microscope (PLM) and take a color photomicrograph, so that any changes in the general appearance of the sample are monitored and recorded during the analytical work. The PLM can provide both a measure of the complexity of the sample from the number of different particle types, and also some compound identification from the optical properties of a particle. In conjunction with the PLM work, a Thermogravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC) scan of the sample is made. This method is used primarily to determine 1) the stability of the sample, and 2) an appropriate temperature at which to dry samples to be used in later tests. In some cases, the compounds present can be determined by weight loss at specific temperatures.

Quantitative anion analysis is performed using ion chromatography (IC). Besides its excellent sensitivity, IC provides survey information on the anions present. Accurate elemental analysis is important for quantitation of the compounds present. Several techniques Atomic Absorption Spectroscopy (AAS), X-Ray Fluorescence (XRF), Particle Induced X-Ray Emission (PIXE), Inductively Coupled Argon Plasma (ICAP), and Neutron Activation Analysis (NAA) are discussed, and recommendations on their use are given.

The following sections provide information on the techniques summarized in Table 4. The information provided is directed at the knowledgeable chemist and is designed to improve his understanding of the uses and limitations of the methods described.

A section discussing the integration of the above methods into a coherent analysis pattern is discussed in the last section of this chapter.

Table 4. Summary of Initial Sample Characterization

Analysis Method	Principle of Operation	Information Derived	Compound Identification Procedure	Limitations
Level 1 Spark Source Mass Spectrometry (SSMS) Data	RF potential used to breakdown sample placed in two electrodes Resultant ions accelerated out of source through electrostatic and electromagnetic analyzers (similar to organic mass spectrometry) Determine mass distribution in resultant ion beam. Use detection system that provides required sensitivity and precision: • Photographic plate system. Used for total characterization of sample since entire periodic table is examined and possible interferring ions are resolved • Electrical detection system. Good for single element determination	Provides elemental concentration data on elements Can determine trace elements in quantities as low as 0.01 ppm Absolute sensitivities range from 1 through 400 ng	Need elemental distribution data to reduce compound choices Elemental information especially useful in interpreting IR and XRD data	Accuracy of analysis typically 100 to 500%. If only Level 1 data is used, could allow a Yes or No answer to the presence of possible compounds
Thermogravimetric Analysis (TGA)/ Differential Scanning Calorimeter (DSC)	TGA records weight loss or gain as material is heated DSC measures heat evolved or absorbed as sample is heated	TGA provides specific information on thermal stability of sample: weight loss can sometimes be correlated with decomposition of specific compounds DSC data gives information on phase transitions or chemical reactions in sample	TGA/DSC normally cannot determine compounds present in complex mixtures without information on elemental and anion composition Primary use in this identification scheme is to provide stable drying temperatures and identify any reactive or volatile materials present	Since small sample sizes are normally used, chemical stability of low concentration materials is not seen The maximum temperature of most instruments is 1000°C, which is below decomposition point of many compounds
Polarized Light Microscope (PLM)	Particles are collected from various sources, crushed to 0.05 mm, and examined with microscope. Of special importance are observations of: • Refractive index (relief) • Isotropy or anisotropy • Birefringence • Pleochroism • Fracture • Color • Crystal habit	At low magnification, general appearance of sample is noted for quality control of sample handling/storage At higher magnification, crystal structure, color, refractive/ index are measured for single particles Initial view indicates minimum number of different particles and their potential compounds	All crystalline compounds have specific refractive indexes which can be used to identify the compound Amorphous materials can sometimes be identified by comparison to known substances via particle atlas	Limited to single particle analysis Trace constituents adsorbed on particles or extremely small particles (0.5μ) must be measured with another technique (SEM-EDX) Homogeneity important for correct identification Results difficult to quantitate

Table 4. Summary of Initial Sample Characterization (Continued)

Analysis Method	Principle of Operation	Information Derived	Compound Identification Procedure	Limitations
Micro-Solubility Tests	View small amounts of sample under PLM while adding cold water, hot water, dilute HCl, and dilute bicarbonate solutions Record information on individual particle solubilities	Solubility of particles in specific solvents indicate the class of compounds present	Use solubility data to verify later results Use solubility data in conjunction with anion micro-spot tests to reduce number of possible compound choices	Micro-tests on a microscope stage require good technique and extreme care Results reflect composition of single particles and not the bulk of the sample
Micro-Spot Tests	Isolate single particles on stage of PLM: • Micro-spot test for specific anions ($SO_4^=$, NO_2^-, NO_3^-, $CO_3^=$, Cl^-) • Compare to quantitative standards	Reveals presence or lack of specific anions	Combination on anion and solubility information limits the number of cations present in sample and aids in single particle compound identification	Micro-tests on microscope stage require good technique and extreme care Results difficult to quantitate
Atomic Absorption Spectroscopy (AAS)	Introduce sample into AAS and decompose with flame or heat or furnace until gaseous metallic atoms are formed Make quantitative determination of amount of metal in sample by comparing level of sample absorbance at specific wavelengths with that of known standards	Provides concentration data on metals With flameless techniques, detection limits between 0.001 and 1 ng are possible for various elements	Specific cations can be identified and quantitated These metals can be correlated with specific particle types Cation information can be coupled with solubility and anion content information to aid in compound identification	Analyses of non-metals and metalloids cannot be performed

2.1 POLARIZED LIGHT MICROSCOPY

Polarized light microscopy (PLM) is the first direct compound analysis method. Many particles can be identified by the determination of such properties as the refractive index, isotropy or anisotropy, birefringence, pleochroism, fracture, color, and crystal habit. An excellent survey article on PLM identification is found in West (18), while a complete discussion of PLM identification procedures is found in McCone (19)

The following sections will provide additional detail about the operation of PLM for screening of the sample and preliminary compound identification.

2.1.1 Theory

Such physical characteristics as color, shape, reflectivity, surface roughness, clarity, size and size distribution of small particles or crystals can be observed under medium magnification in a conventional optical microscope. In some cases, these data may be sufficient to identify a sample compound. If not, the use of polarized light microscopy (PLM) can provide additional data which may permit direct identification, particularly with crystalline materials. Crystals can be divided into three clases (Figure 3) based on the number of refractive indices observed under polarized light. Crystals with one refractive index (RI) will remain dark when rotated under crossed polarized filters and are termed anisotropic. Crystals with two RI's (uniaxial and isotropic) or three RI's (biaxial anisotropic) appear to flash when rotated under crossed polarized filters.

Determination of the RI of the crystal can be made via an immersion technique with an error of ±0.001 units. This is often enough to permit exact identification of the compound, particularly when a second and possibly third RI are determined. Table 5 lists the RI's of a variety of compounds which may be encountered in environmental analysis to illustrate the range of RI's commonly encountered.

When a tentative identification has been made, chemical verification can be performed under the microscope. In most cases, there are standard wet chemical qualitative analysis (20) procedures performed on a single crystal or small group of particles. For example, solubility in a

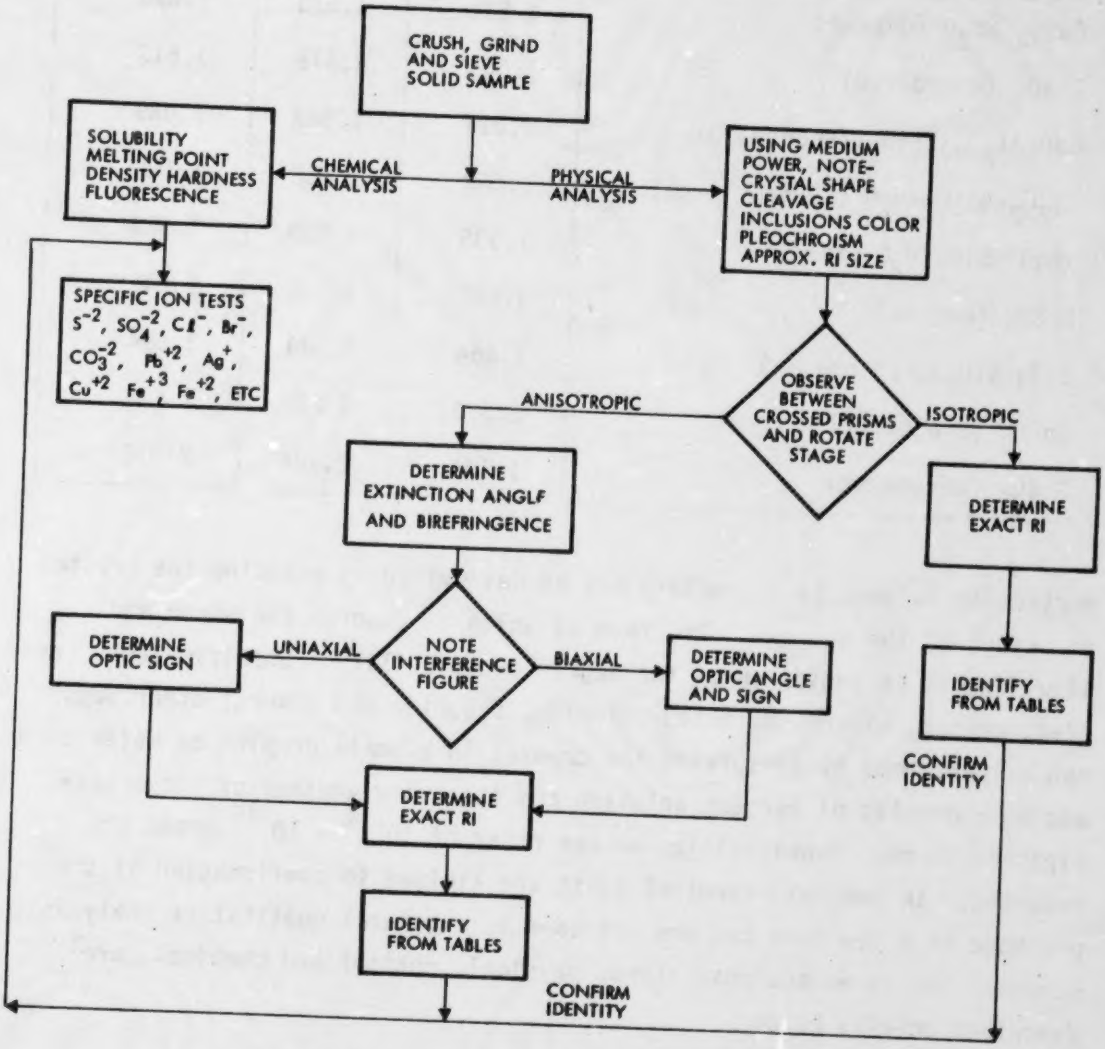
CRUSH, GRIND AND SIEVE SOLID SAMPLE
CHEMICAL ANALYSIS
PHYSICAL ANALYSIS
SOLUBILITY MELTING POINT DENSITY HARDNESS FLUORESCENCE
SPECIFIC ION TESTS S^{-2}, SO_4^{-2}, Cl^-, Br^-, CO_3^{-2}, Pb^{+2}, Ag^+, Cu^{+2} Fe^{+3}, Fe^{+2}, ETC
USING MEDIUM POWER, NOTE- CRYSTAL SHAPE CLEAVAGE INCLUSIONS COLOR PLEOCHROISM APPROX. RI SIZE
OBSERVE BETWEEN CROSSED PRISMS AND ROTATE STAGE
ANISOTROPIC
ISOTROPIC
DETERMINE EXTINCTION ANGLE AND BIREFRINGENCE
DETERMINE EXACT RI
NOTE INTERFERENCE FIGURE
UNIAXIAL
BIAXIAL
DETERMINE OPTIC SIGN
DETERMINE OPTIC ANGLE AND SIGN
IDENTIFY FROM TABLES
CONFIRM IDENTITY
DETERMINE EXACT RI
IDENTIFY FROM TABLES
CONFIRM IDENTITY

Figure 3. Identification of Single Particles Using Polarized Light Microscopy (PLM)

Table 5. Refractive Indices of Selected Crystals (N_d^{25})

Biaxial Anisotropic			
Crystal	RI alpha	RI beta	RI gamma
$CaSO_4 \cdot 2H_2O$ (gypsum)	1.521	1.523	1.530
$CaSO_4$ (anhydrite)	1.569	1.575	1.613
$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (anorthite)	1.516	1.583	1.589
$Al_2O_2 \cdot 4SiO_2 \cdot H_2O$ (pyrophyllite)	1.552	1.588	1.600
$3MgO \cdot 4SiO_2 \cdot H_2O$ (talc)	1.539	1.589	1.589
$BaSO_4$ (barite)	1.637	1.638	1.649
$CaMg(SiO_3)_2$ (diopside)	1.664	1.671	1.694
$CaCO_3$ (aragonite)	1.530	1.681	1.685
$PbCO_3$ (cerussite)	1.804	2.706	2.078

particular solvent (e.g., water) may be determined by exposing the crystal to vapors of the solvent. The rate at which it absorbs the vapor and liquifies is an indicator of the degree of solubility. Specific tests for lead, copper, silver, sulfate, chloride, fluoride and several other ions can be performed by dissolving the crystal in a small droplet of water then adding a droplet of reagent solution and observing whether or not a precipitate forms. Sensitivities on the order of 10^{-14} - 10^{-15} grams are reported. In general, chemical tests are limited to confirmation of the presence of a few ions and are not used as a general qualitative analysis scheme. The three analysis steps, physical, optical and chemical, are described briefly below.

2.1.2 Compound Identification - Generalized Procedure

Sample Preparation

Solutions should be evaporated and the solid material crushed. Solid samples can be crushed or milled to obtain particles of approximately 50 μm diameter. Samples are mounted on microscope slides and held by any conventional powder support (tacky Canada balsam, immersion oil, etc.).

Liquid samples for chemical analysis should be placed in a slotted microscope slide and covered with a cover slide.

Physical Analysis

Using medium power, note the crystal shape and number and orientation of cleavage planes. Using these observations, assign a crystal habit if possible (cubic, columnar, platy, spherulitic, needle-like, fibrous, etc.). Note any inclusions of gas or solid in the particle or crystal. Using ordinary white light, observe the color of the sample. Few common inorganic compounds are colored and this is therefore an important observation. In anisotropic substances, rotation of a beam of polarized light may cause the color to vary with the orientation of the light plane, a phenomenon termed pleochroism. Note whether the material is pleochroic. If so, more than one refractive index will be observed. If the material has not been crushed, observe and record the particle size by comparison with standard grids or an ocular scale. If the particle or crystal has not been identified from these observations, proceed to optical analysis.

Optical Analysis

To determine whether the substance is isotropic or anisotropic, polarizing light filters are placed between the light and sample and between the sample and ocular. If the crystal (e.g., NaCl, cubic) remains dark when rotated in the field of polarized light, it is isotropic, possessing only one refractive index. Completion of the characterization of isotropic substances requires only the determination of the refractive index. Anisotropic crystals will change color or flash when rotated in the cross-polarized beam. Anisotropic or birefringent crystals can be further divided into two classes, which are analyzed separately (Figure 3).

One of the basic optical characteristics of birefringent crystals is the so-called interference figure, which serves to subdivide the anisotropic group into two classes, uniaxial and biaxial. One method for locating interference figures is to focus on the field, cross the prisms, remove the ocular and move the slide until an interference figure appears. This is usually the most rapid method when the particles are randomly oriented. The interference figure for a uniaxial crystal appears as a dark Maltese cross extending across the field. Concentric rings of colors (isochromatic curves) may also be present. The interference figure for a biaxial crystal consists of hyperbolic curves which move in and out as the stage is rotated.

Light passing through uniaxial anisotropic (or doubly refractive) crystals is broken into two rays traveling at different velocities. For uniaxial crystals, these rays are known as the ordinary (ω) and extraordinary (ϵ) rays. The sign is determined by whichever ray has the greater index, such that, $\epsilon - \omega$ = birefringence, the sign of which is called the "optic sign."

The determination of the refractive indices of a uniaxial crystal requires that the crystal be properly oriented in polarized light; the individual indices are then resolved and are determined in the same manner as for an isotropic crystal. In general, uniaxial crystals show two refractive indices when placed in positions of extinction between cross prisms. The indices are measured focusing on a field of a few crystal fragments using low intensity parallel light and a 4-mm or 8-mm objective. The analyzer is inserted, a crystal showing maximum birefringence is selected and centered, and the stage is rotated until the crystal is dark (extinction). The analyzer is then removed and the index is estimated by comparison with the known index of the mounting medium using the Becke line method. The analyzer is again inserted, the stage rotated to the second position of extinction, and the other index is estimated. This procedure is repeated using appropriate mounting media until at least two or three checks are obtained for the higher and lower indices. If the crystal is uniaxially positive, the lower index value will be that of the ordinary ray, while if the crystal is negative, the higher value will be that of the ordinary ray.

The identification of biaxial crystals by conoscopic methods resembles closely the procedure described above for uniaxial crystals, the main difference being that three refractive indices are determined. In addition, biaxial crystals have another property, the optic angle, which can be measured readily and used as an aid in identification. When an interference figure is obtained which indicates that a crystal is biaxial, it is used to determine the optical character as was done in the case of uniaxial crystals. Further, it may be used for the estimation of the optic angle and the preliminary estimation of the intermediate index of refraction (β). The final measurement to be made is the determination of the three refractive indices.

Refractive Index

The determination of refractive indices for biaxial crystals is complicated by the fact that there are three different indices. These indices are represented by N_p, N_m, and N_g, (petty, medium, great), or more commonly by α, β, and γ. To determine these indices, their order of magnitude is first estimated by the degree of relief in Shillaber's oil or Canada balsam. The α and γ indices are then determined by locating a crystal of optimum birefringence, rotating to extinction, and determining the index by means of the Becke line method (18). The crystal is then rotated to the second position of maximum extinction and the second index determined. By repeating this procedure with appropriate immersion liquids until the highest and lowest indices have been established, the values for γ and α will be obtained. For a biaxial positive crystal, β will have a value nearer the index. If it is biaxial negative, β will be nearer the α index. It is of value to note that crystals having optic angles approaching zero degrees will have a value approaching either α or γ values, and crystals with optic angles near 90° will have a β index almost half-way between the other indices. The value of β is estimated from the values determined for α and γ, the optic sign, and the optic angle.

Chemical Analysis

Confirmation of the chemical composition of a sample particle or crystal may be obtained by microchemical analysis. The crystal is dissolved by exposure to a saturated vapor of the solvent, usually water. These tests, called Chamot-type precipitation tests can be found in detail in reference 20.

2.1.3 Typical Results from PLM

As part of a Comprehensive Assessment of an industrial boiler equipped with a wet scrubber and capable of being oil- or coal-fired, PLM analyses were performed on samples taken at the inlet and outlet of the wet scrubber.

The samples from both an oil firing and coal firing boiler consisted of an EPA M-5 train with a cyclone and filter at the inlet and an EPA M-5 train with only a filter at the outlet. During coal fired tests, flyash samples from a mechanical precipitator were also taken and analyzed.

Table 6 shows the type of results possible from PLM. Information on weight, modal diameter and size range was obtained from most of the samples. Only outlet filters were not completely analyzed because of the low amount of material and their hydroscopic nature.

Particles found in most samples were flyash, partially fused flyash, oil soot, and iron oxide (hematite and magnetite). Traces of quartz, shards, coke, and calcite were found in many samples. Both scrubber cake samples contained calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2H_2O$) which was the principal component of sample 202-4-scrubber cake. The presence of an unknown sulfate in the outlet filter during the coal fired tests was a strong indication that the scrubber was adding scrubber liquor reactive products ($NaHSO_3$) to the outlet mass loading, and this was later confirmed from the elemental FTIR and XRD studies.

Regardless of whether coal (series 201) or oil (series 202) was used to fire the boiler, oil soot was found in the samples collected. The oil soot found during the oil tests was largely in the form of complete cenospheres with smooth, unbroken walls. Oil soot from sample 201-1-flyash which is representative of the oil soot in all the 201 series samples appears to be broken, abraded, and has a grainy surface texture. The more worn appearance of the 201 series oil soot indicates that it was probably oil soot retained in the ducts from some earlier oil combustion. Knowing this information, chemical analysis of the coal samples would be corrected for the affect of the oil soot.

Table 6. PLM Analyses Results

COAL FIRED BOILER SAMPLES

Components	201-1-Flyash			201-1-1-Cyclone			201-1-1-Filter			201-1-Scrubber Cake			201-1-0-Filter
	A	B	C	A	B	C	A	B	C	A	B	C	A
Partially fused flyash	65-80%	30	5-140	55-70%	25	5-65	40-55%	12	5-40	55-70%	20	4-60	
Flyash	1-5%	4	1-20	10-20%	4	1-16	35-50%	2	<1-13	10-20%	5	1-15	
Oil soot	5-15%	25	2-100	10-20%	15	2-80	10-25%	8	1-40	10-20%	15	1-60	25-40%
Magnetite	10-20%	12	3-45	10-20%	12	3-25	<2%	5	2-14	1-5%	10	5-45	
Iron oxide	2-5%	15	1-40	1-5%	7	<1-50	<2%	5	1-18	<2%	3	1-21	15-25%
Coke	1-5%	40	5-160	<2%	60	6-100							
Quartz	<2%	12	5-60	<2%	20	5-40							
Calcite										<1%	6	1-10	1-5%
$CaSO_3$-1/2H_2O										10-20%	6 (length)	3-21 (length)	
Unknown sulfate													50-65%

OIL FIRED BOILER SAMPLES

Components	201-4-I-Cyclone			202-4-I-Filter	202-4-Scrubber Cake			202-4-0-Filter
	A	B	C	A	A	B	C	A
Partially fused flyash	25-35%	20	6-40					
Flyash	1-5%	3	<1-15					
Oil soot	50-75%	20	<1-140	10-20%	1-5%	30	1-80	
Magnetite	<2%	12	3-50					
Iron oxides	<1%	8	3-35	15-30%				5-10%
Unknown sulfate	1-5%			45-60%				50-65%
$CaSO_3$-1/2H_2O					95%+	30	2-80	
Calcite				1-5%				
Water droplets				15-30%				30-45%

Key: A - Estimated weight percent
B - Estimated modal diameter (μm)
C - Size range (μm)

2.2 THERMAL ANALYSIS

This section describes a number of methods which measure some property of the material as a function of temperature. The primary methods discussed will be Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (22-29)/(DSC). These tests will primarily be used to determine the thermal stability of the sample so that a safe drying temperature can be selected.

2.2.1 Principles of Operation

Thermal analysis is a general term for techniques which measure physical changes in material occurring upon a change in temperature. Common physical changes which can be monitored include changes in weight, length or specific heat of a sample.

The most frequently used measurements can be categorized into the six techniques listed in Table 7. Of these, the first three are the principal techniques to be used in a Level 2 analyses scheme.

Table 7. Thermal Analysis Techniques

Method	Function	Temperature Range (°C)
Differential Scanning Calorimetry (DSC)	Measures heat flow into or out of a sample	-180-725
Thermogravimetric Analysis (TGA)	Measures sample weight changes	Ambient to 1200
Differential Thermal Analysis (DTA)	Measures temperature excursions of a sample	-180-1600
Thermomechanical Analysis (TMA)	Measures sample dimensional changes	-160-1200
Evolved Gas Analysis (EGA)	Measures specific evolved sample decomposition products	Variable by technique
Dynamic Mechanical Analysis (DMA)	Measures sample modulus and damping changes	-150-500

TGA is concerned with the weight change of a sample as the temperature is increased in a prescribed manner. Differential thermal analysis involves the measurement of changes in heat content as a function of the temperature difference between the sample and a thermally inert reference material as both substances are heated, or cooled, at identical, well-controlled rates. The results of such an analysis allow a measurement of melting points, vaporization points, crystal phase transitions, chemical changes and other enthalpic changes. The weight changes accompanying any of these changes are determined by TGA.

The instrumentation for a TGA consists of a precision balance, a furnace which can be programmed for reproducible temperature changes over a specified time period and a recorder. There is generally a reaction chamber in the furnace which enables an analysis to be performed in atmospheres other than ambient air, e.g., inert, or under vacuum. Either a null-point or a deflection type of balance is acceptable. The recording system should provide a continuous record of weight and temperature to ensure a complete description of thermogram features. Furnace design and controls must be capable of providing a satisfactory, smooth input so that either a linear heating program (typically 10° - 600°C/hr.) or a fixed temperature can be maintained over an operating range up to at least 1100°C.

A DTA contains four basic elements: 1) a sample holder with a dual thermocouple assembly, 2) a furnace and its controller, 3) a flow control system and 4) a recorder. As with the TGA, the furnace must be able to be controlled to provide a reproducible, constant heating or cooling rate, over a range of about 0° to 30°C/min. Again a desirable maximum operating temperature is about 1000°C.

Differential scanning calorimetry differs from DTA in the respect that the difference in power required to maintain the sample and the inert reference material at the same temperatures as they are heated or cooled is measured. The DSC contains two separately heated sample holders--for the sample and the reference. A power difference will be observed whenever physical or chemical changes occur in the sample: this power difference represents the thermal energy absorbed, or released, as a consequence of the changes in the sample. The temperature of each is measured with resistance thermometers. Here too a means of assuring a steady, reproducible, well-controlled temperature change is essential.

2.2.2 Applications and Methodology

In the Level 2 analysis thermogravimetry will be most often used to determine the drying ranges of materials and the most suitable drying conditions to be used before weighing samples and proceeding with other analyses. The most useful information will be obtained by using either a slow heating rate or several different heating rates in an inert atmosphere.

A sample thermogram of the changes calcium oxalate monohydrate undergoes during heating is shown in Figure 4.

The plateaus on the TGA graph indicate the sample is maintaining a constant weight; that is, the sample is stable in that particular temperature range. Inflections represent such physical or chemical changes as water or solvent loss, formation of another compound, or sorption of volatile materials in the sample.

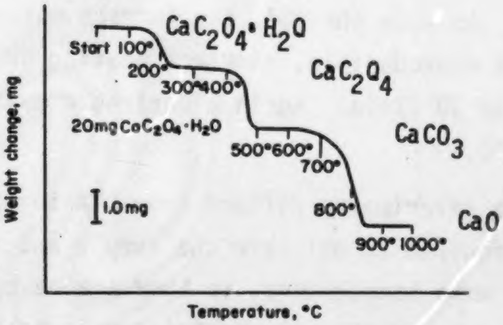

Figure 4. Thermogravimetric Evaluation of Calcium Oxalate Monohydrate; Heating Rate 6°C/min.

In interpreting data from a TGA or DTA analysis, consideration must be given to the apparatus and to the procedure used. Variations due to the dynamic nature of the method are very possible. In particular, there is often little correlation between results from isothermal (run at single temperature) runs and non-isothermal (temperature scan) runs.

The shape of the TGA or DTA curve is affected by the heating rate, the nature of the sample and its container and the atmosphere in which the analysis was done. At a given temperature, the extent of change in the sample varies inversely with the heating rate. A slow heating rate further helps to differentiate rapid, successive changes. A small, finely divided sample will behave more uniformly and reproducibly.

This result is demonstrated in Figures 5 and 6, which show the DSC of >3 μm material collected at the outlet of a limestone wet scrubber.

The Figure 5 run at 10°C/minute shows three large endothermic peaks at 87°C, 120°C, and 190°C with several smaller shoulders at 140°C and 230°C. The major peaks roughly correspond to the dehydration of $CaSO_3 \cdot 1/2H_2O$ (100°C), $CaSO_4 \cdot 2H_2O$ (to the half hydrate - 128°C) and $CaSO_4 \cdot 1/2H_2O$ (163°C).

An attempt was made to resolve these shoulders by reducing the amount of sample and greatly reducing the heating rate. A heating rate which is too high or too large a sample would prevent rapid equilibration of the sample and would cause the response to changing temperatures to lag. This fact is illustrated by the improved resolution obtained in Figure 6. The scan is quite different, showing peaks at 47°C, 94°C, 160°C, and shoulders at 115°C and 175°C. The 47°C peak is probably due to surface water and baseline drift. Clearly, the 94°C and the 160°C peaks correspond to the $CaSO_3 \cdot 1/2H_2O \rightarrow CaSO_3$ and the $CaSO_4 \cdot 1/2H_2O \rightarrow CaSO_4$ dehydrations. The shoulder at 115°C might be due to the dehydration of $CaSO_4 \cdot 2H_2O$. The 175°C shoulder is unidentified, but may represent a phase change of $CaSO_4$ between α and β forms or a reaction of an unidentified material.

Once a compound is tentatively identified, it is possible to use the peak area under a DSC curve to calculate the ΔH of the reaction and use it to identify the compound present. Conversely, if the compound is known, then the ΔH can be used to quantitate the compound. Assuming that the

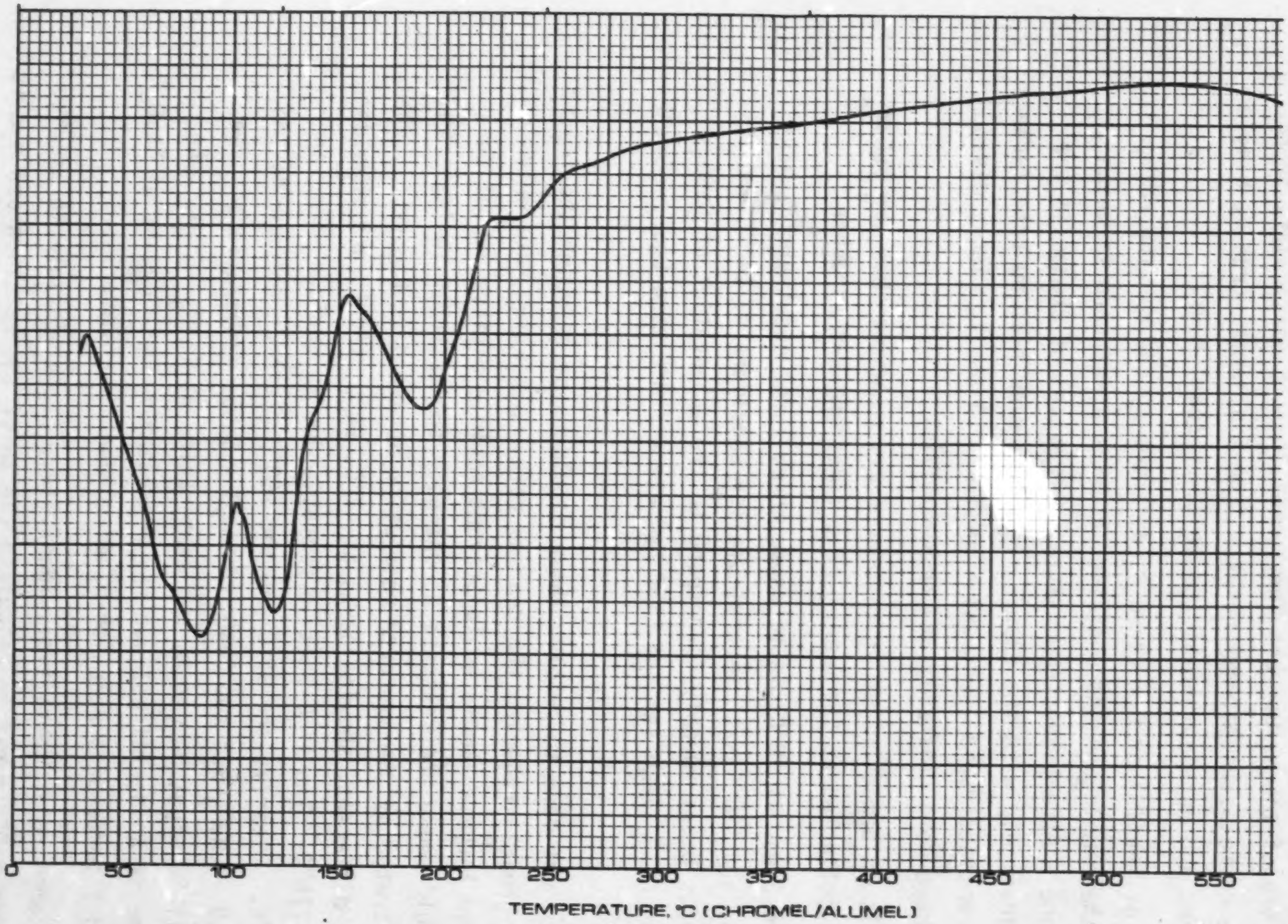

Figure 5. DSC of >3 μm Material Collected at the Outlet of an FGD Run at 10°C/min.

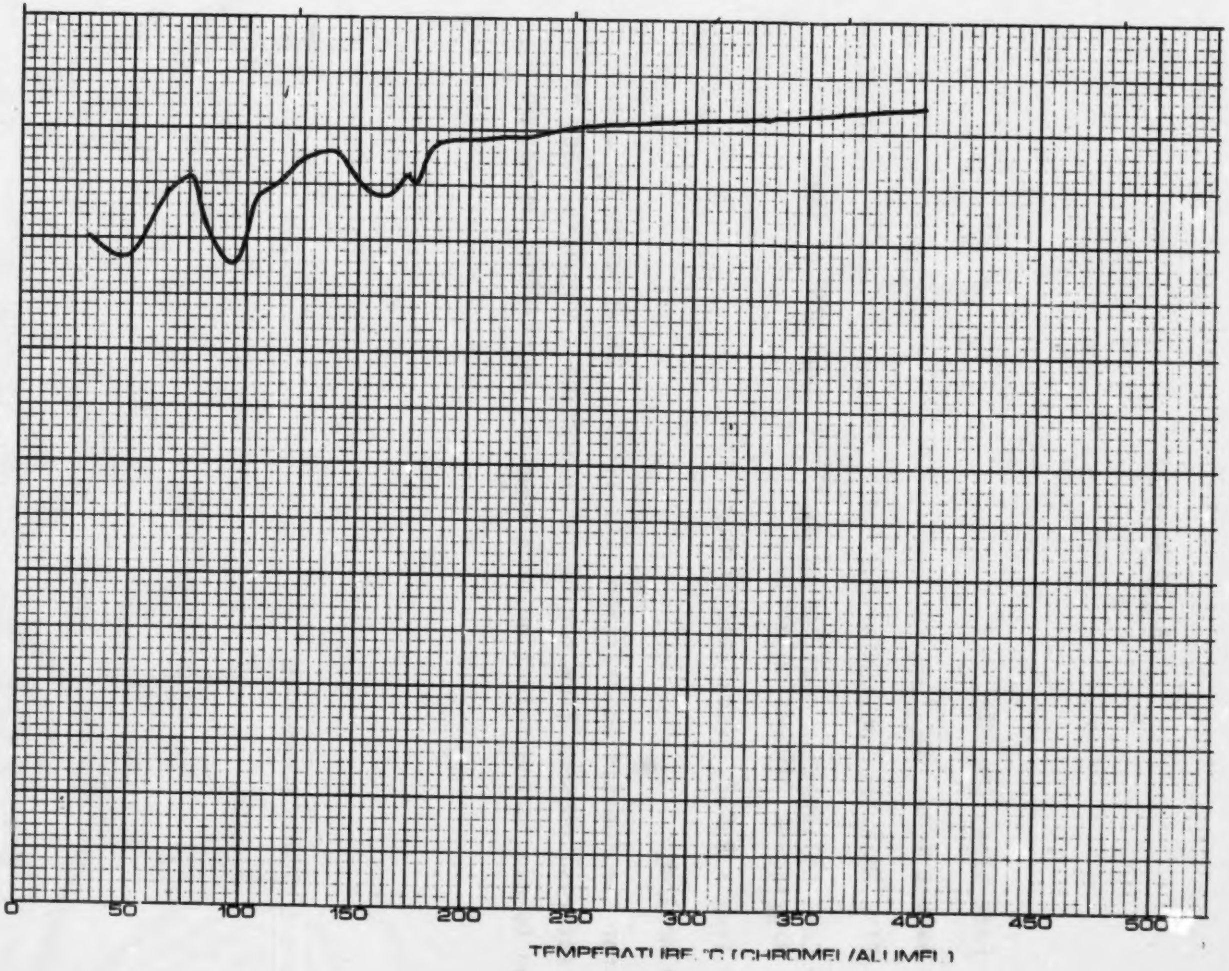

Figure 6. DSC of >3 μm Material Collected at the Outlet of an FGD Run at 2°C/min and Reduced Sample Size.

94°C and 160°C peaks are due to dehydration of $CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 1/2H_2O$, respectively, it is possible to calculate the material present if the ΔH of the dehydration is known. The formula for this calculation is:

$$m = \frac{A\ (60\ BE\ \Delta qs)}{\Delta H}$$

where

A = Peak area, (sq. in.)

m = Sample mass, (mg.)

B = TIME BASE setting, (min/in.)

E = Cell calibration coefficient at the temperature of the experiment (dimensionless).

Δqs = Y-axis RANGE, ((mcal/sec.)/in.)

ΔH = mcal/mg

If the ΔH for the identified reaction is available, an estimate of the amount of material present from the DSC will provide a valuable piece of information to aid in the selection of a compound identification method.

2.3 ANION ANALYSIS

The analysis of samples for anions is a necessary first step to quantitate the compounds that might be present. The anion data and the elemental analysis data can be compared on a mole basis to determine if the elements and anions make a match.

Anion data will also expand or modify the potential compound list developed in Chapter 1. The recommended method of analysis for most samples is ion chromatography on the basis of sensitivity, accuracy, and flexibility. Included in this manual are specific anion tests for all the anions expected in environmental samples. The following sections will describe the use of IC for anion analysis.

2.3.1 Specific Tests

Anions are commonly analyzed individually using wet chemical procedures. Sample preparation procedures must be selected which do not contaminate the sample prior to analysis. Samples dissolved in aqua regia, for example, cannot be analyzed for nitrate or chloride. In general, aqueous samples may be analyzed directly and most anionic species are water soluble in their common forms (except oxides and most phosphates). In Appendix A, procedures are given for the individual analysis of aqueous samples, bromide, iodide, carbonate, bicarbonate, cynaide, fluoride, nitrate, nitrite, orthophosphate, sulfide, sulfite, sulfate, and ammonia. Most of these quantitative tests have been taken from the EPA "Manual of Methods for Chemical Analysis of Water and Wastes". A procedure for the analysis of samples for ammonia is included in this section although this species is usually present as a cation in aqueous media. Sample collection and preparation procedures, detection limits, and potential interferences are given.

2.3.2 Ion Chromatography

The chromatographic separation of anionic (and cationic) components of a sample has been refined recently (30,31). Ion chromatography (IC) instruments are commercially available which can analyze for the following anionic species: acetate, arsenate, bromide, carbonate, chloride, fluoride, iodide, nitrate, nitrite, orthophosphate, sulfate, sulfite (and ammonium). Typical parameters for analysis of aqueous sample for these species by IC are given in the following section.

IC Theory

Conventional ion exchange chromatography (32) involves the separation of ions based on the differences in their rates of exchange with similarly charged ions bonded to stationary ions of the opposite charge on a resin. Sample ions of interest are placed at the head of the column and eluted with a mobile phase, or eluent, which contains similarly charged ions. The function group, at the active site of a resin, is always opposite in charge to the exchanging ions. The rate at which the ions exchange positions is determined by the ion's attraction to the functional group. The physical characteristics of size and charge determine the ion's attractions or interaction with the functional group or resin. Ions which have a charge that can be polarized toward the functional group will have a stronger interaction with the resin, thus a slower rate of exchange.

When ions elute from the resin, they are in a background of the mobile phase ions. Modern ion chromatography is a process which employs an anion or cation ion-exchange column followed by a second acid or base ion-exchange column. The first column is called the separator and is usually a low capacity column. The second column, called the suppressor, neutralizes the mobile phase and is usually a high capacity column. The neutralization of the mobile phase ions allows the eluting sample ions to be detected by simple conductivity. Ion chromatography can be applied to the analysis of samples for acetate, bromide, chloride, fluoride, iodide, nitrate, nitrite, orthophosphate, sulfate, sulfite, (and ammonia, as well as other cations).

Sample Preparation

The sample is extracted with hot distilled water extraction to remove all of the soluble anions. The same sample is then extracted with a 0.1N HNO_3 solution to solubilize the remaining anions. This approach will solubilize most of the common anions (Cl^-, $SO_4^=$, NO_3^-, Br^-, I^-, PO_4^{-3}), but the analyst must be aware of potential problems with species like $SO_3^=$ and $CO_3^=$. Species like $CaSO_3$ would be insoluble in water and would oxidize or volatilize in HNO_3. If CO_3 or $SO_3^=$ are suspected to be present in the solid then gas evoluation by HCl addition, followed by a dilute NaOH trap is recommended. In both cases air must be excluded to prevent $SO_3^=$ oxidation and CO_2 absorption. Both anions can be run in the NaOH solution using the columns shown in Table 8.

Application of Ion Chromatography to Environmental Analysis

Samples from the venturi/spray tower (limestone) scrubber at the EPA/TVA Shawnee Test Facility in Paducah, Kentucky and the Arthur D. Little Alkali Pilot Scrubber were analyzed by ion chromatography.

The anions of interest for both dual alkali and lime/limestone wet scrubbers are: sulfite, sulfate, carbonate, chloride and nitrite. The anion analysis procedure was developed by TRW based on the Dionex instruction manual but modified (33) to optimize the separation and response in the matrices encountered at lime/limestone wet scrubbers. Table 8 summarizes the analytical conditions needed for analysis of the cations and anions found in wet scrubbers.

The Detection Limit (DL) for sulfite, sulfate and nitrite is one ppm; carbonate is 5 ppm whereas chloride could vary between 0.1 and 10 ppm depending on conditions. In the chloride analysis, the DL improves if eluent is added to the sample before analysis. The addition of eluent to the sample suppresses the water dip on the ion chromatogram which occurs immediately before the chloride peak. Carbonate usually has a high DL due to carbonate found in the blanks.

The analytical scheme is based on the retention time for sulfate which is the last species of interest to elute from the columns. The conditions stated below will cause sulfate to elute in 15 to 17 minutes, but the sulfite and nitrate peak will be only partially resolved. Conditions can be changed so that sulfite and nitrate will be completely resolved, but the retention time of sulfate increases to about 45 minutes. Wet scrubber samples have little nitrate, however, and the incomplete sulfite and nitrate resolution is not a problem. Because sulfite is constantly oxidizing to sulfate, the shorter analysis time is preferred.

Quantitative analysis may be performed using either peak height or peak area; however, a series of experiments have shown that peak height is better than peak area due to variations in peak shape and detector response

Table 8. Retention Time of Various Ions Found in Wet Scrubbers

Species	Conc.	Retention Time	Dionex Separator Column	Dionex Suppressor Column	Flow Rate	Elluent	Temp.
Cl^-	10 ppm	4.5 min	Anion 3 x 500	Anion 6 x 250	30%	0.003M $NaHCO_3$/ 0.015M Na_2CO_3	24°C
$SO_3^=$	10 ppm	10	Anion 3 x 500	Anion 3 x 500	30%	0.003M $NaHCO_3$/ 0.025M Na_2CO_3	24°C
NO_3^-	10 ppm	8	Anion 3 x 500	Anion 3 x 500	30%	0.003M $NaHCO_3$/ 0.025M Na_2CO_3	24°C
$SO_4^=$	10 ppm	16	Anion 3 x 500	Anion 3 x 500	30%	0.003M $NaHCO_3$/ 0.025M Na_2CO_3	24°C
$CO_3^=$	10 ppm	6	Bio Rad 6 x 500	None	30%	Water	24°C
Ca^{+2}	10 ppm	12	Cation 6 x 250	Cation 9 x 250	40%	for both cations 0.001 M p-phenylenediamine dihydrochloride	24°C
Mg^{+2}	10 ppm	8	Cation 6 x 250	Cation 9 x 250	40%		24°C
Na^+	10 ppm	7	Cation 6 x 250	Cation 9 x 250	40%	0.005N HNO_3	24°C
K^+	10 ppm	12	Cation 6 x 250	Cation 9 x 250	40%	0.005N HNO_3	24°C

characteristics. Figure 7 is an ion chromatogram of a solution which contains F^-, Cl^-, NO_2^-, PO_4^{-3}, Br^-, NO_3^-, and SO_4^{-2}. Each ion has its own basic shape/ F^- and Cl^- are sharp spikes where as SO_4^{-2} is a broad Gaussian. Calibration curves are constructed by running standard solutions of known ion concentration on the ion chromatograph and determining peak heights. A plot of sample concentration vs peak height is constructed. Figure 8 shows that the linear range for Cl^- ions is from less than 1 ppm to 10 ppm. The calculation of the slope of the curve is determined by a "least squares" fit of the data points.

The accuracy and precision of the analytical scheme was tested using samples from the lime/limestone wet scrubber at the EPA/TVA Shawnee Test Facility in Paducah, Kentucky. Table 9 shows a direct comparison between TVA and TRW sample analyses of lime/limestone wet scrubber samples for Cl^- and SO_4^{-2}. The relative error for each set of values is listed as well as results of an alternate analysis employed as a check. The chloride ion values were very consistent for both analytical techniques employed. Because of most chlorides solubility, those compounds would be less susceptible to changes in ph, and as a result would not be expected to vary. The data confirmed that as the relative differences between the reported values ranged from 1.8% to 4.5%.

2.4 BULK ELEMENTAL ANALYSIS

The results from the Level 1 SSMS will provide specific information on the number of elements present in the sample and approximate (factor of 2-3) concentrations. Elements exceeding their MATE values will be analyzed more accurately. The choice of the final Level 2 elemental analysis method will be left to the individual analyst. This decision will be influenced primarily by the in-house or local vendor capabilities. The following sections will provide an overview of elemental analysis procedures with the emphasis on understanding their use and limitations. The methods discussed are: Atomic Absorption Spectroscopy, Atomic Fluorescence Spectroscopy, Neutron Activation Analysis, X-Ray Fluorescence and Proton Induced X-Ray Emission.

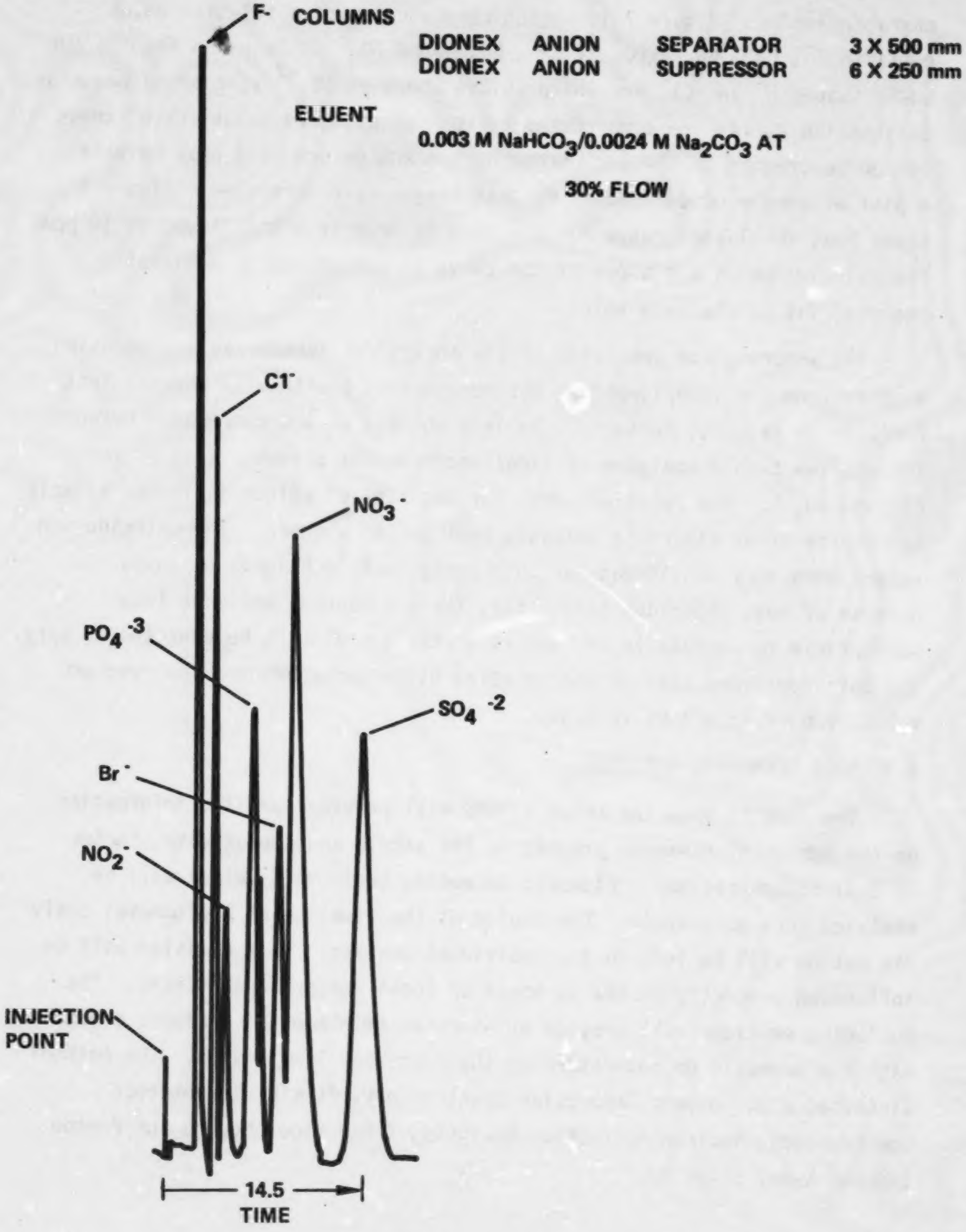

Figure 7. Ion Chromatogram of the Dionex Anion Standard Solution

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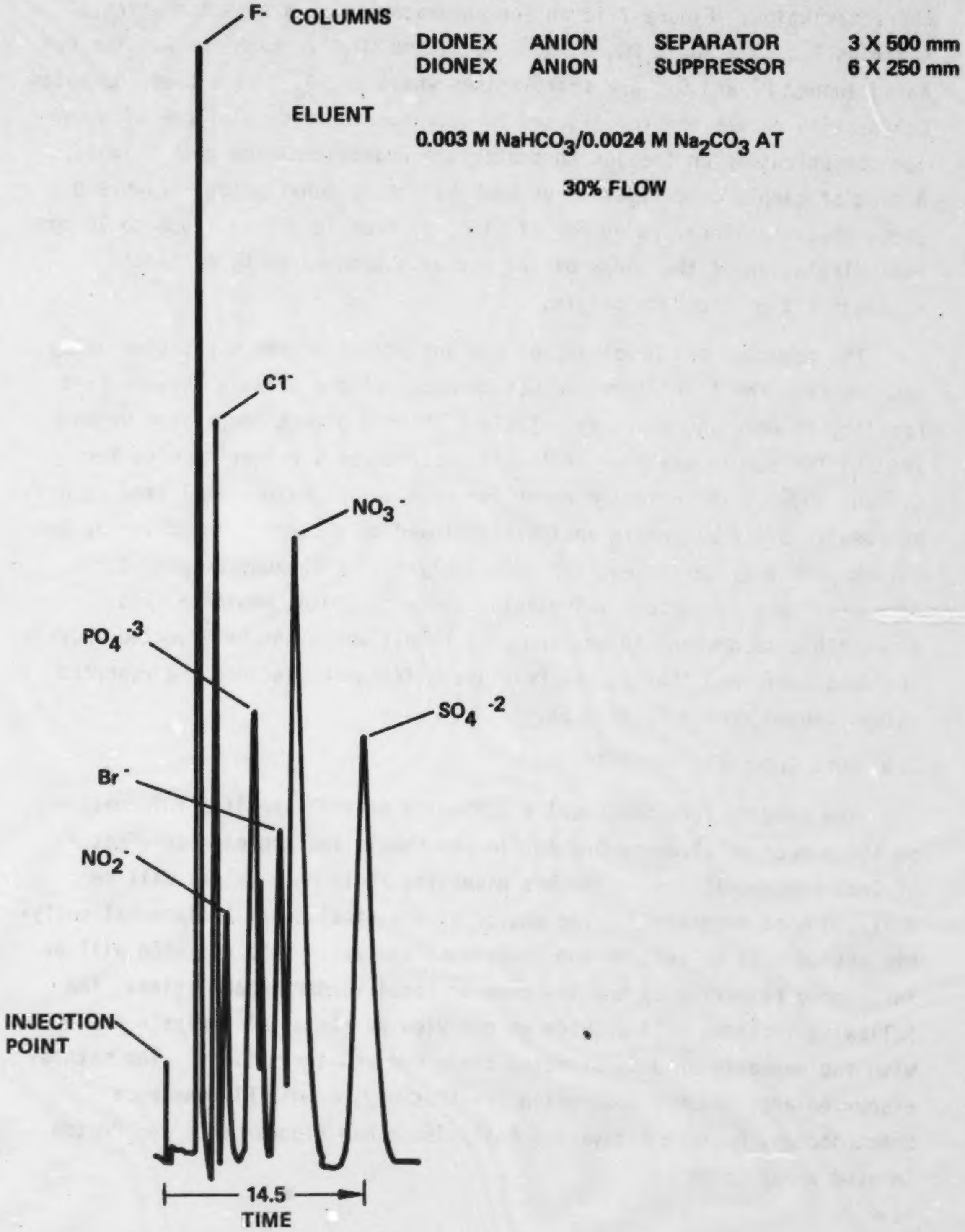

Figure 7. Ion Chromatogram of the Dionex Anion Standard Solution

Table 9. Comparison of SO_4 and Cl Analysis Methods

		#5253		#5254		#5255		#5256	
Species	Method of Analysis	Conc.	Rel. Error	Conc.	Rel. Error	Conc.	Rel. Error	Conc.	Rel. Error
Sulfate	Ion Exchange (TVA) Ion Chromatography (TRW)	32994 34000	3%	17584 16209	8%	17700 16660	6%	31442 34404	9%
Chloride	Potentiometric (TVA) Ion Chromatography (TRW)	2676 2726	2%	1418 1454	3%	1418 1485	5%	2614 2675	2%

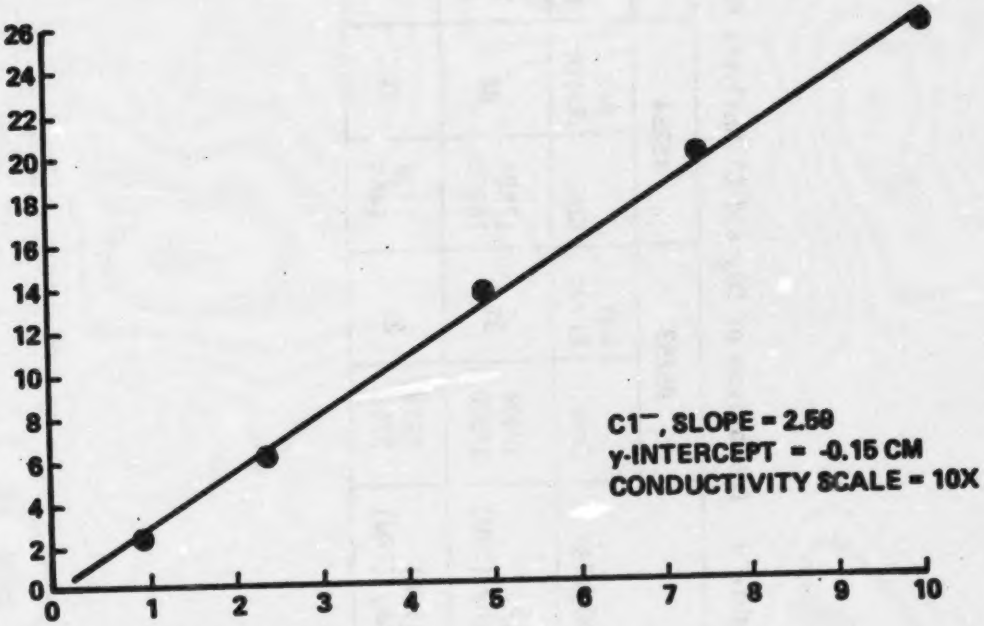

Figure 8. Calibration Curve for Chloride Ion Analysis

2.4.1 Introduction-Atomic Techniques

The electronic structure of each element is unique, and only specific energies will cause excitation of an electron from the atomic ground state to a higher energy level. On return to the ground state, the excess energy is given off at an energy which again is specific for that element. Several analytical techniques have been developed which exploit this elemental specificity. These are schematically shown in Figure 9. Atomic absorption spectroscopy (AAS) uses the technique of measuring the absorption of light from a monochromatic source (hollow cathode lamp) by a particular element or measuring the absorption at a given wavelength from the spectrum of a continuum source (Xe lamp or H_2 hollow cathode lamp). Atomic fluorescence spectroscopy measures the light emitted from an element returning to its ground state after excitation by a hollow cathode lamp or continuum source. Atomic emission spectroscopy uses the emission produced as electrons return to the ground state following thermal excitation by a flame or plasma. Each of the techniques is applicable to approximately 60 elements. Their advantages and limitations will be discussed below and the methods compared as to their sensitivity and applicability to multi-element analysis. Methods of preparing samples for analysis by these techniques are presented in Section 2.5.4.

2.4.1.1 Atomic Absorption (AAS)

The analysis of a sample by AAS requires the following steps: introduction of the sample, evaporation of the solvent, atomization (conversion to the atomic ground state) and measurement of the absorption of light. Two techniques exist for the first three steps. Conventional AAS aspirates

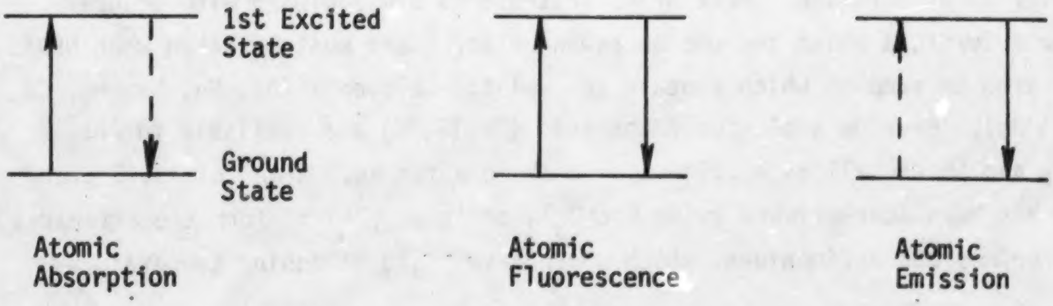

Figure 9. Schematic of Atomic Techniques

the aqueous sample into a flame (FAAS) where thermal energy evaporates the solvent and decomposes compounds to atoms. In the so-called "flameless" techniques (NFAAS), an aliquot of the sample is placed in a furnace, the solvent removed by heating at low temperature, and the sample subsequently atomized by rapid heating of the furnace. The light source for either system is commonly a hollow cathode lamp whose cathode is constructed of the element(s) to be analyzed and filled with an inert gas (Ne or He) at low pressure. As current is passed through the cathode, atomic emission lines are produced, characteristic of the composition of the cathode, further enhancing specificity. The absorption of this light by the element in the sample follows Beer's Law over a given concentration range. Monochromators are used to select the analytical wavelength for measurement by a photomultiplier/amplification system. The signal from the hollow cathode is usually chopped or modulated and the detector synchronized to the chopped signal. In this way the DC signal due to other emissions (the flame itself or molecular emission from compounds formed in the heating chamber) can be electronically suppressed.

Potential Problems in NFAAS and FAAS

FAAS requires larger sample volumes per analysis (1 to 5 ml) than NFAAS (0.1 to 0.5 ml). Furthermore, factors affecting viscosity of the sample (and thus the flow rate of the sample into the flame) such as the presence of organic solvents or high solid content require special attention when standards are prepared for FAAS analysis. The method of standard additions is recommended for most analyses of complex matrices by both FAAS and NFAAS. The presence of condensed vapors or smoke from residual organic material drastically reduces the precision of NFAAS analysis. Therefore, following evaporation of the solvent, samples must be ashed in the furnace prior to atomization. Most NFAAS instruments are equipped with programmable furnaces which include an ashing step. Care must be taken when NFAAS is used on samples which contain the volatile elements (As, Se, Sb, Hg, Cd, and Pb). Hydride evolution techniques (34,35,36) are available for As, Se, and Sb as well as a cold vapor technique for Hg. NFAAS of As, Se, and Se has been accomplished using $Ni(NO_3)_2$ addition (34) to form the arsenides, selenides and antimonides, which are non-volatile at ashing temperatures.

The efficiency of atomization is reduced in some cases by ionization of the analyte to a state other than its atomic ground state. This can be overcome by the addition of a substance with preferentially ionizes. Formation of compounds (oxides, phosphates) which do not decompose to atoms in the flame or furnace also decreases sensitivity. Use of higher temperatures can often overcome the problem (nitrous oxide/acetylene flames in FAAS) as will the addition to the sample of a substance which will inhibit oxide or phosphate formation (lanthanum, for example). In some cases, spectral interferences can occur. For example, analysis for small amounts of the transition metals in an iron matrix would require pretreatment of the sample. In other cases, using the method of standard addition may be sufficient.

Application to Multielement Analysis

The spatial requirement that the light source and detector be placed at 180° reduces the applicability of single element hollow cathode lamps in both flame and flameless AAS. True simultaneous analysis exists for only a limited number of elements (usually two) where multiple source/detector pairs are focused on the sample chamber. Multi-element (2 to 4) hollow cathode lamps can be used to analyze samples sequentially by use of a scanning monochromator and a single detector. The intensity and lifetime of these lamps is usually less than that of single element lamps.

Use of continuum sources to excite several elements which are analyzed by programmed scanning has been successful to a limited extent. The power output of these lamps (Deuterium hollow cathode lamps and to a lesser extent Xenon arcs) is significantly lower than the elemental hollow cathode lamps, thus their sensitivity is higher. Using a continuum source for FAAS or NFAA, excitation parameters must be set at the lowest common denominator for the elements being observed, further reducing the sensitivity for the other elements. For the above reasons, it is recommended that AAS not be used for multi-element analysis. AAS can best be used for selected elemental analysis requiring high accuracy (±10%) or when a limited number of elements is analyzed.

2.4.1.2 Atomic Fluorescence (AFS)

The instrumental requirements for AFS are essentially those of AAS, usually flame, with the difference that the fluorescence signal is measured at right angles to the excitation path. For spatial reasons, AFS is more conducive to multi-element analysis since detectors can be placed anywhere along a plane perpendicular to the incident beam. Thus use of multiple monochromator/detector systems permits true simultaneous analysis. Furthermore as with all fluorescence techniques the intensity of the emission is proportional to the intensity of the incident beam. Use of electrodeless discharge lamps (EDL's), which have greater output than hollow cathode lamps, increases sensitivity in fluorescence systems. The applicability to multi-element analysis is restricted by the same considerations as discussed for AAS, namely, the need for an excitation source for each element or a lower power continuum source. Potential problems in analysis by AFS are the same as those discussed for AAS, and, in addition, commercial units are not readily available.

2.4.1.3 Flame Atomic Emission Spectroscopy

In atomic emission spectroscopy the excitation source is the flame itself. Thus, the principal drawback of source/detector orientation in AAS and AFS is eliminated. Since the emission occurs in all directions, a theoretically unlimited number of single element monochromator/detector systems could be configured around the flame. In practice, however, it is more common to use a single detector and scan the emission spectrum with a monochromator. Programmable scanners allow preselection of given wavelengths for study and the monochromator is rapidly moved between the chosen "windows." Thus, selectivity and multiple element capability exist in AES. Another advantage of emission techniques is that they are linear over several orders of magnitude in concentration (up to the limit where self absorption occurs) whereas fluorescence techniques are linear over about three and absorption methods to a limit of about two orders of magnitude concentration change.

Its principal drawback, however, has been the lack of sensitivity due to the high background emission of the flame itself. Broadband emissions make the flame spectrum complex and variations in the flame introduce severe noise problems not present in AAS. Use of flames which have lower backgrounds improves the sensitivity of the technique. The most promising approach to solving this problem, however, has been the use of non-combustion flames, or plasmas.

Interferences in AES

As with other atomic techniques, sensitivity of the method is affected by formation of refractory oxides, electron transfer reactions due to the presence of easily ionizable elements (the alkali metals), factors which affect viscosity of the sample, changes in flame composition or temperature. The method of standard additions is recommended for most analyses.

2.4.1.4 Inductively Coupled Argon Plasma Spectroscopy (ICAP)

Inductively coupled argon plasma spectroscopy (37,38,39,40,41,42) is essentially a "flame" emission technique where the excitation source is a plasma torch whose temperature is on the order of 7000°K. An inductively coupled plasma is maintained by a high-frequency, axial magnetic field in a laminar flow of argon at atmospheric pressure. The discharge gas in the induction-coupled plasma is pure argon, which reduces background signal significantly. In order to maintain very high temperatures without wall contamination, a laminar flow of cold argon surrounds the plasma.

The atomization system usually consists of a pneumatic nebulizer which allows the introduction of solutions of various concentrations and of any degree of acidity or viscosity. Organic solvents may be employed if the sample container is made of an appropriate material. The argon flow rate is the primary factor controlling the rate of addition of aerosol to the plasma. Droplet size of the aerosol will be affected by viscosity, surface tension, and sample depth.

Signals are monitored with dual channel monochromators, one set to monitor atomic emissions and the other to monitor plasma emissions to correct for background. A commercial instrument using a single light dispersion device (grating) and a mask which focuses set emission lines onto 40 dedicated photomultipliers is available.

Interferences in ICAP

Inter-element effects can be minimized by proper selection of plasma geometry. Since the elements in the sample are in an essentially inert atmosphere, interferences from chemical reactions should be minimal. Refractory oxides or phosphates can still form and reduce sensitivity as with all techniques requiring atomic ground states. Electron transfer reactions can occur in the presence of easily ionizable substances (the alkali metals), reducing sensitivity for some metals. Matrix effects are minimal when proper background correction, mentioned above, is employed. Memory effects are problems inherent in the instrument. Because of the high temperature of the plasma torch, an analyte may adsorb on the wall of the sample tube tip when the plasma gas is turned off. This memory effect can be reduced by cleaning the sample tube tip with HNO_3 solution at the beginning of a new start-up. A second memory effect, located in the nebulizer, is caused by the analyte solution creeping down both the gas and sample needle and away from the tip. The analyte solution clinging to the outside of the needles may be gradually dislodged as it is replaced by the succeeding blank solution causing a positive interference.

Another problem is that many elements have complicated emission spectra. For example, Fe has an extremely rich emission spectra under the conditions that exist in the plasma. It is quite possible that the emission lines chosen for the other elements lie very close to an Fe emission line. If the monochromator cannot distinguish between the two lines, a spectral interference results and the instrument gives a reading that is too high because of the presence of the iron emission line. Spectra inferences can be further compounded by the fact that most commercial ICAP units use fixed photomultipliers which limits the ability to select alternate lines to avoid spectral overlap.

2.4.1.5 Comparison of the Methods

Minimum detectable quantities (detection limits) can be used as an indication of the applicability of a method to a particular analysis. Table 10 lists order-of-magnitude detection limits for FAAS, NFAAS, and ICAP. As a screening method ICAP offers the best combination of sensitivity and multielement capability. For the exact determination of a particular element, atomic absorption is the method of choice owing to the availability

Table 10. Comparative Detection Limits (ppb) (μg/L)(42)

Element	ICP[10]	Flame AA	Furnace AA
Al	10	20	0.004
As	15	100	0.06
B	2	1000	
Cd	1	1	0.008
Co	2	5	0.03
Cr	2	3	0.005
Cu	2	2	0.008
Fe	1	5	0.003
Mn	0.5	3	0.004
Mo	5	10	0.06
Ni	5	8	0.02
P	30	10^5	3.0
Pb	15	10	0.03
Pt	20	50	0.45
Se	15	100	0.10
Si	10	60	0.10
Ti	1	50	0.30
U	75	7000	
V	2	20	0.15
Zn	1	0.6	0.0007

of instruments, their specificity and sensitivity. The methods are simlar in sample preparation requirements and potential interferences. Due to the greater amount of work in the AAS area, this method is the method of choice for single element analysis.

2.4.1.6 Application of AAS and ICAP to Environmental Analysis

As part of an environmental assessment (43) conducted on samples from a Fluidized Bed Combustion (FBC), a comparison of AAS and ICAP recoveries was conducted. Weighed particulate samples from the fluidized bed combustor were transferred to Teflon-lined Parr digestion bombs and digested overnight at 130°C with 5 mL of aqua regia. The resulting solutions were filtered through Whatman No. 41 filter paper. The collected residue was ignited, fused with 1 g of high purity sodium carbonate Na_2CO_3, dissolved, combined with the original filtrate and diluted to 50 mL. Leachate samples were prepared through 24 hour refluxing extractions in a solution of hydrochloric acid at pH 4 and a basic colution of ammonium hydroxide at pH 9. Undissolved particulates were removed by filtration and were not recovered for further analyses. The AAS instrument employed for this analysis was a Jarrell-Ash 810 equipped with an FLA-10 Graphite Tube Furnace. The procedures listed in Table 11 were chosen to meet the Level 2 accuracy requirements of ±15%.

ICAP analyses were conducted using an Applied Research Laboratories (ARL) prototype instrument, Model QA-137, on all the leachate solutions. In general, the detection limits are on the order of 0.01 μg/mL, although they vary from element to element and from matrix to matrix. Standard additions of Al, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K and Ba were made to each leachate to assess matrix effects and recovery. Calibration of the instrument was accomplished using reagent salts diluted with deionized water.

Tables 12 and 13 summarize the spike recovery data for AAS and ICAP respectively. Both methods showed excellent recoveries from both the acidic and basic leachate solutions. ICAP has the added benfit of analyzing all the elements reported at a cost less than one twentieth of the AAS.

Table 11. Atomic Absorption Analytical Operating Parameters

Element	Analytical Wavelength, Å	Background Wavelength, Å	Slit Width, Å	Atomization Source	Analytical Procedure
Ag	3281	3235 (Ne)	10	G.F.*	Dry – 30 sec. @ 200°C Ash – 60 sec. @ 400°C Atomize – 7 sec. @ 2300°C – Argon Gas
Cu	3247	None	10	G.F.*	Dry – 30 sec. @ 200°C Ash – 60 sec. @ 600°C Atomize – 6 sec. @ 2500° C – Argon Gas
Ni	2320	2316	4	G.F.*	Dry – 20 sec. @ 200°C Ash – 30 sec. @ 800°C Atomize – 6 sec. @ 2800°C – Argon Gas
Li	6708	None	2	Air-C_2H_2	Atomic Emission
Mg	2852	None	4	Air-C_2H_2	Atomic Absorption
Pb	2833	2825	4	G.F.*	Dry – 40 sec. @ 200°C Ash – 40 sec. @ 600°C Atomize – 6 sec. @ 1900°C 10 μl 1.0% HNO_3 & 0.2% $(NH_4)_6Mo_7O_{24}$ added in furnace
Zn	2139	None	4	Air-C_2H_2	Atomic Absorption
Hg	2536	None	10	Flameless	$SnCl_2$ reduction N_2 Sparge 1 1/min
Cd	2288	None	4	Air-C_2H_2	Atomic Absorption
Be	2349	None	4	N_2O-C_2H_2	Atomic Absorption
Cr	3579	None	4	Air-C_2H_2	Atomic Absorption
Pt	2659	Continuum	4	G.F.*	Dry – 30 sec. @ 300°C Ash – 30 sec. @ 1150°C Atomize – 5 sec. @ 2700°C – Argon Gas
V	3185	3196	2	G.F.*	Dry – 30 sec. @ 200°C Ash – 40 sec. @ 1000°C Atomize – 5 sec. @ 2800°C – Argon Gas
Si	2516	None	2	N_2O-C_2H_2	Atomic Absorption
Sr	4607	None	2	Air-C_2H_2	Atomic Emission

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*Graphite furnace.

Table 12. Percent Recovery of Spiked Samples by Atomic Absorption

Element	Solutions		
	Leachates		
	Acid	Basic	Particulate
Zn	104	105	-
Mg	-	-	95
Ag	80	80	78
Ni	60	110	-
Li	104	103	-
Cu	80	80	-
Cd	-	-	110
Be	100	100	100
Cr	-	-	84
Pb	105, 97	93	130, 84
Pt	100	64	-
V	113	107	116
Si	96	122	107
Hg	100	100	102
Sr	75	80	106
Average Recovery	93.4	95.3	101

Table 13. ICAP Recovery Results, %

	Fe	K	Mg	Mn	Al	B	Ba	Ca	Cu	Cd	Co	Cr	Mo	Ni	Average Recovery
Acidic Leachates	94.05	98.4	94.0	93.0	94.9	100.3	103.0	96.5	94.5	91.1	96.6	97.7	94.5	97.2	96.1
Basic Leachates	74.1*	102.0	95.2	94.3	95.1	94.0	112.0	104.3	97.4	96.7	96.3	92.7	94.2	105.1	96.7

*$Fe(OH)_3$ was observed as a precipitate

2.4.2 Neutron Activation Analysis

Neutron activation is another alternative to provide accurate multi-element analyses of environmental samples (45 through 54). The method is based on the radiochemical reactions possible when an element is exposed to a flux of neutrons. When exposed to a flux of thermal neutrons, many elements will undergo a nuclear reaction (neutron capture) creating another nuclide according to the reaction:

$$^{M}_{Z}A \xrightarrow{(n)} {}^{M+1}_{Z}B + \gamma$$

with the immediate emission of electromagnetic radiation. Subsequent decay of the product (B) produces gamma ray emission at discrete wavelengths. Monitoring of these characteristic gamma rays provides a selective and sensitive method for determining the composition of an unknown sample. Quantitative analysis via NAA requires the knowledge of several constants and experimental values including: the activation cross-section for A, the half life of B, the neutron flux, the irradiation time and the delay time following removal from the flux and prior to analysis.

The most commonly used and most intense neutron sources are provided by neutron chain reactors utilizing the fission reaction. Fast neutrons (>1 Mev) produced by the fission of uranium are moderated to epithermal (~0.4 ev) and further to thermal (<0.4 ev) energies. These thermal neutrons assure continuation of the fission reaction but can also be used to produce artificial radioactivity, induced when a target material is exposed to thermal energies. In order to determine accurately the flux to which the sample is exposed, a standard is irradiated simultaneously with, and as near as possible to, the unknown sample. A relative counting of the standard and sample is performed and the unknown weight is calculated as follows:

$$(g)u/(g)S = (A)u/(A)S$$

where (g)u and (g)S are the weights of unknown and standard, and (A)u and (A)S are count rates of unknown and standard, respectively. Many potential sources of errors can be eliminated by irradiating the sample with a standard of similar composition. When the composition of a substance is unknown, a preliminary irradiation should be performed and can be used as a qualitative analysis in order to fabricate a suitable standard. Care should be taken that the sample and standard are approximately the same weight, shape and thickness.

Analysis of the gamma ray spectrum from a sample is usually performed using a high resolution lithium-drifted germanium (GeLi) detector connected to a multi-channel analyzer. Most facilities provide for direct computer analysis of the spectrum. Using this method, multi-element analysis can be performed on a single sample.

Detection Limit

The sensitivity of NAA for a given element depends on the isotopic abundance of the stable isotope (which becomes the radioactive isotope), the cross section for neutron capture of the stable isotope, the available neutron flux, the length of irradiation, the half-life of the radioactive isotope produced, the decay scheme of the radioactive isotope, the decay period before counting, the efficiency of the radiation detector for the type of radiation being measured, and interference from other elements in the sample. The latter can be eliminated by pre- or post-irradiation chemical separation of the interferent. Some optimized detection limits are given in Table 14.

For multi-element analysis, however, the irradiation scheme can be far from optimum for some elements since half-lives can vary from a few minutes to several years. For complete analysis two irradiations are required. First, a short irradiation followed by immediate analysis for the short-lived components (Al, Ca, Cu, S, Ti, Cl, Br, Mg, Mn and In) is performed. A subsequent analysis for elements with longer half-lives (K, Zn, Ga, W, Sb, La, Sm, Eu, Au, Cr, Se, Co, Fe, Se, Ag, Ce, Hg, Th and Ni) requires a longer irradiation time (several hours) followed by a cooling period (to eliminate short-lived emissions) of 20 hours and analysis of elements with half-lives of 8-50 hours. A further cooling period of 20-30 days is required prior to analysis for elements whose half-lives are longer than 10 days.

Interferences:

As with other multielement techniques, matrix problems can be encountered. Preparation of standards whose matrix is similar to the

Table 14. Detection Limits Reported For Some Elements By Neutron Activation Analysis (55)

Atomic Number	Element	Detection Limit, µg	Atomic Number	Element	Detection Limit, µg
11	Na	0.0003	47	Ag	0.0003
12	Mg	0.01	48	Cd	0.0004
13	Al	0.0005	49	In	0.000003
14	Si	3.0	50	Sn	0.001
16	S	7.0	51	Sb	0.0002
17	Cl	0.003	52	Te	0.002
19	K	0.01	53	I	0.00001
20	Ca	0.1	55	Cs	0.00005
21	Sc	0.001	56	Ba	0.0003
22	Ti	0.004	57	La	0.0004
23	V	0.00004	58	Ce	0.01
24	Cr	0.05	59	Pr	0.002
25	Mn	0.000004	60	Nd	0.0006
26	Fe	10.0	62	Sm	0.00003
27	Co	0.0003	63	Eu	0.000003
28	Ni	0.02	64	Gd	0.0006
29	Cu	0.0001	65	Tb	0.003
30	Zn	0.008	66	Dy	0.000002
31	Ga	0.0001	67	Ho	0.00007
32	Ge	0.003	68	Er	0.0001
33	As	0.0002	69	Tm	0.03
34	Se	0.002	70	Yb	0.0005
35	Br	0.0001	71	Lu	0.00002
37	Rb	0.02	72	Hf	0.001
38	Sr	0.0001	73	Ta	0.05
39	Y	0.02	74	W	0.0002
40	Zr	0.1	75	Re	0.00006
42	Mo	0.005	77	Ir	0.00002
44	Ru	0.001	78	Pt	0.01
45	Rh	0.0001	79	Au	0.00001
46	Pd	0.002	80	Hg	0.01

sample is important. Interelement interferences can be eliminated by pre- or post-irradiation chemical treatment but is not usually required.

Sample Preparation

Solids usually require little or no sample preparation. A known quantity is sealed in a polyethylene or quartz container and irradiated. Liquid samples may be run directly or evaporated onto a surface prior to being sealed in a container. Some care must be taken that the container can withstand the temperature of the irradiation area and that expansion of the sample on heating does not cause it to rupture. In samples where the matrix contains large amounts of a potential interferent, pretreatment to remove the element (ion exchange, precipitation, etc.) is advised.

2.4.3 X-Ray Fluorescence Analysis-Introduction

When exposed to the proper amount of energy, many elements will undergo excitation of an inner core electron. Upon cascading of the remaining electrons to fill the hole created, X-rays are emitted, the wavelengths of which are characteristic of the element. This forms the basis for the techniques of Energy Dispersive X-ray Fluorescence (EDXRF or XRF) (References 56-65) and Particle Induced X-ray Emission (PIXE) (Reference 66-73). The two methods are distinguished by the excitation technique and are discussed separately below.

2.4.3.1 XRF (Theory)

In conventional X-ray fluorescence, X-rays are used as the excitation source. An X-ray tube or a radioactive source of X-rays is used as a primary (continuum) source of radiation. X-ray tubes have the advantage of greater power and therefore lower sensitivity. The broadband radiation from this source is usually focused onto a target of a pure metal (Cu, Mo, Ti or Sm) to produce a coherent X-ray beam which is then focused on the sample. Use of such secondary sources reduces background due to coherent and incoherent scattering of the continuum source radiation. A disadvantage of the selective secondary source excitation technique is that the number of elements excited by the secondary X-ray beam is reduced since excitation efficiency is highest when the exciting energy just exceeds the binding energy of the electron in a given atomic shell. For this reason, multiple analyses are usually performed using, for example, titanium secondary emitters for elements of atomic numbers 13-20, molybdenum for elements 20-38 (plus lead and mercury) and samarium for elements of atomic numbers 38-56. One approach to monitoring X-rays from the samples is to use a solid state lithium-drifted silicon detector coupled to a multichannel analyzer. Another system common employed is wavelength dispersion. In this system the secondary X-rays from the sample are directed onto a crystal. These X-rays are diffracted by the crystal according to the Bragg equation. The separated X-rays are detected using a proportional or scintillation counter which is rotated through 180°.

Sample Preparation

Proper sampling procedures can eliminate the need for sample preparation. Collection on a thin film (e.g., Teflon, Mylar, cellulose) allows direct sample analysis. Sealing a known quantity of a solid material between two thin films or evaporation of an aliquot of a liquid sample onto a thin film or filter is usually sufficient.

Interferences

Absorption of the X-rays from the sample by the support medium (filter or thin film) may be significant for elements below 10 in atomic number when they are imbedded in a substrate. Use of Mylar or membrane filters, where the sample remains on the surface can significantly reduce this problem. Further, these substrates have low mass and thickness, reducing background count. Self-absorption is only a problem for elements above potassium and then only when present in large amounts (e.g., >200-400 $\mu g/cm^2$). Since particle size and sample thickness may be significant in elements below atomic number 20 (calcium), the accuracy of analysis for these elements varies widely, depending on the size, thickness, and composition of the sample. For elements below calcium, wavelength dispersive XRF, with its higher resolution and lower background, is recommended.

Interferences due to the overlap of X-rays from one element with another may be significant when one is present in large excess. Typically, multiple lines result from a single element, corresponding to filling of holes in the K and, for the heavy metals, L electron shells. The lead $L\alpha_1$ for example will overlap with the arsenic $K\alpha_1$. Such interferences may be eliminated by placing filters between sample and detector, use of a secondary source which does not excite both elements, or mathematical subtraction of the interfering line following analysis for the interfering element from its characteristic X-ray.

Detection Limits

Detection limits for the elements above calcium in atomic number are in the range of 1-10 ng/cm^2 of irradiated surface. The detection limit depends on the background count rate, however, and therefore varies with substrate and sample composition. Detection limits for the elements of atomic number in the range of 21-50 are typically within a factor of two of each other. Use of wavelength dispersive XRF can increase sensitivity a factor of two for most elements, but is usually employed when sample composition is known. For a comprehensive evaluation of detection limits by element and instrument, see reference 65.

2.4.3.2 Particle Induced X-Ray Emission (PIXE)

An alternative method for the excitation of samples for X-ray analysis is the use of accelerated particles, usually protons. Proton beams of 2-5 MeV at a current of 10-50 amps produce the same effect as observed in X-ray fluorescence. The beam may be supplied by an accelerator or cyclotron and detection and amplification is similar to that discussed above. This technique is limited to thin samples or small amounts of sample mounted on a thin support (usually Mylar, Teflon or cellulose acetate). With thicknesses of more than approximately 1 mg/cm^2, appreciable background continuum causes reduced sensitivity. Furthermore, energy losses as the beam passes through the sample and support become significant when the sample is greater than about 10 μm diameter. The high sensitivity of the method compensates for the need to use small samples, and has been used to advantage in analysis of size fractional samples of aerosols from volumes as small as 30 liters of air.

Interferences

The single most important interference is due to energy loss and scattering in thick samples. Particle size becomes important, since self absorption of the X-rays may occur. As with XRF, overlap of L lines from the heavier elements with K lines from the lighter ones may be reduced by filtering or other techniques. Sophisticated computer techniques are usually employed for data analysis.

Detection Limits

The detection limits for the approximately 15 elements which can be detected quantitatively by PIXE are in the microgram region; however, the value depends on the element and the matrix, since the detection limit depends on the cross section of the element and the magnitude of background continuum.

Application of PIXE to Sized Particle Samples

In recent years the amount of trace elements emitted from industrial processes has begun to be a major concern of government sponsored research. Because there is a relationship between size of the particle and its penetration into the lower respiratory system, research has been directed at finding methods to measure the trace element content of sized particles.

Some investigators have simply collected gross quantities of sample, and used sieving techniques to fractionate it (74). This approach always runs the risk of modifying the sample through the sampling or fractionation process, consequently leaving in doubt the true gas phase particle composition. By sampling with an impactor and analyzing the individual stages for trace element content, both mass and elemental concentrations can be calculated (75).

A variety of impactors is available for sampling flue gas streams. In a recent test conducted by TRW an MRI 1502 impactor was used to collect the particles on a greased (Apiezon L) substrate (Kapton film) placed on each collection stage. Only a portion (typically one impaction spot) was mounted in a plastic photographic slide mount for PIXE analysis by Crocker Nuclear Laboratory of the University of California at Davis. In practice two or more impaction spots are sent for analysis. These impactor studies were performed at a coal-fired power plant at the outlet of a limestone scrubber with a venturi/absorber combination using Chevron type mist eliminators.

The impactor data was reduced using the procedure (76,77) developed by Southern Research Institute (SoRI) for IERL/RTP. In this approach $\left[dM/d(\log D_{50})\right]$ the data are normalized so that a smooth curve can be drawn through the limited number of data points obtained from the impactor. The normalized data mass placed in the dM/d (log D_{50}) format is shown in Figure 10. The data for Run 135 was corrected for a negative filter weight using the weight percentage of the filter from Run 136. The filter data point for 135 is shown in brackets. Even without this correction the data agree rather well. The slight offset in the cut points is due to the difference in flowrate between the two runs. In both cases the data show a bimodal distribution with an apparent maximum around 0.4 to 0.5 μm.

In contrast to the mass data, the elemental data obtained from PIXE analysis show maxima at slightly different particle sizes (Figure 11). Other elements were detected, but only the elements with PIXE data for all stages were presented. Calcium, Pb, Zn and Si had a maximum at 20μ and 0.9μ while S was the only element to show a maximum at 0.5μ. Iron showed its concentration maximum over the mass minimum. The lower particle size maximum for the elements corresponds closely to the total mass value (0.4μ to 0.5μ).

It was found that the total elemental weight (even corrected for oxygen) was well below the mass weight found in the stages. If significant amounts of organic material were present, then the total elemental weight would be low due to the insensitivity of PIXE to carbon. A Thermogravimetric Analysis (TGA) in air of outlet fly ash produced no significant weight loss which would occur if organic carbon were present. Additional work with sized standards and mounting procedures is required to improve the absolute accuracy of PIXE in this application.

In order to avoid this apparent problem, the elemental data can be ratioed to Si (a major constituent of fly ash) to attain a relative concentration per stage. The assumption here is that any analysis error would affect all elements in the same fashion. Figure 12 summarizes impactor/PIXE data handled in this fashion. Sulfur showed a consistent enrichment through all the stages and back-up filter. The apparent enrichment on the filter might be due to H_2SO_4 being collected by the final filter, since the impactor in these tests was run at stack temperatures, which would not prevent the collection of H_2SO_4 aerosols. Calcium shows a weak positive trend while Pb and Fe showed a moderately strong trend to increasing concentration at smaller particle size. Zinc showed the strongest trend of

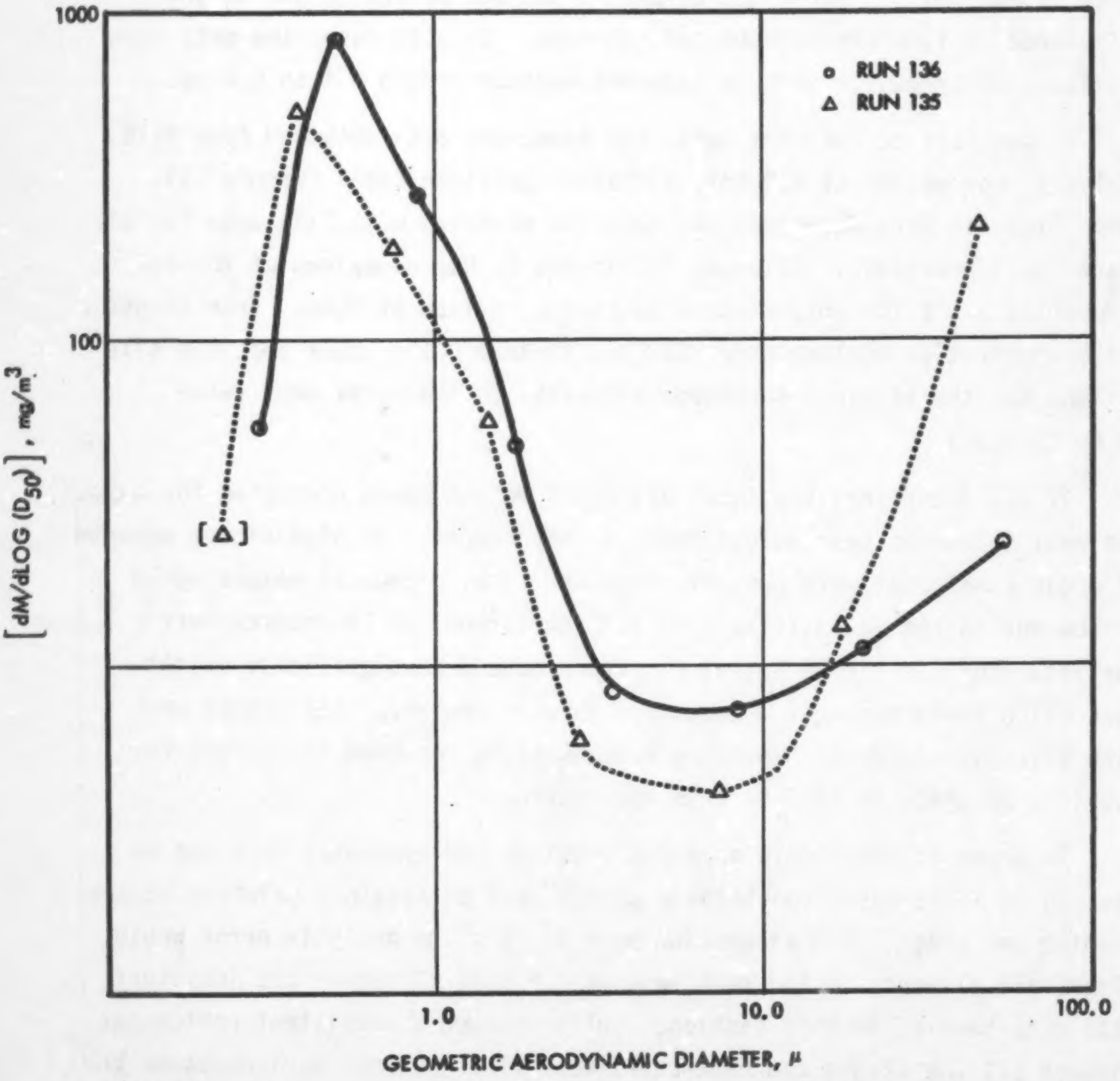


Figure 10. $dM/d(\log D_{50})$ Size Distribution at the Outlet of a Limestone Wet Scrubber at a Coal-Fired Utility

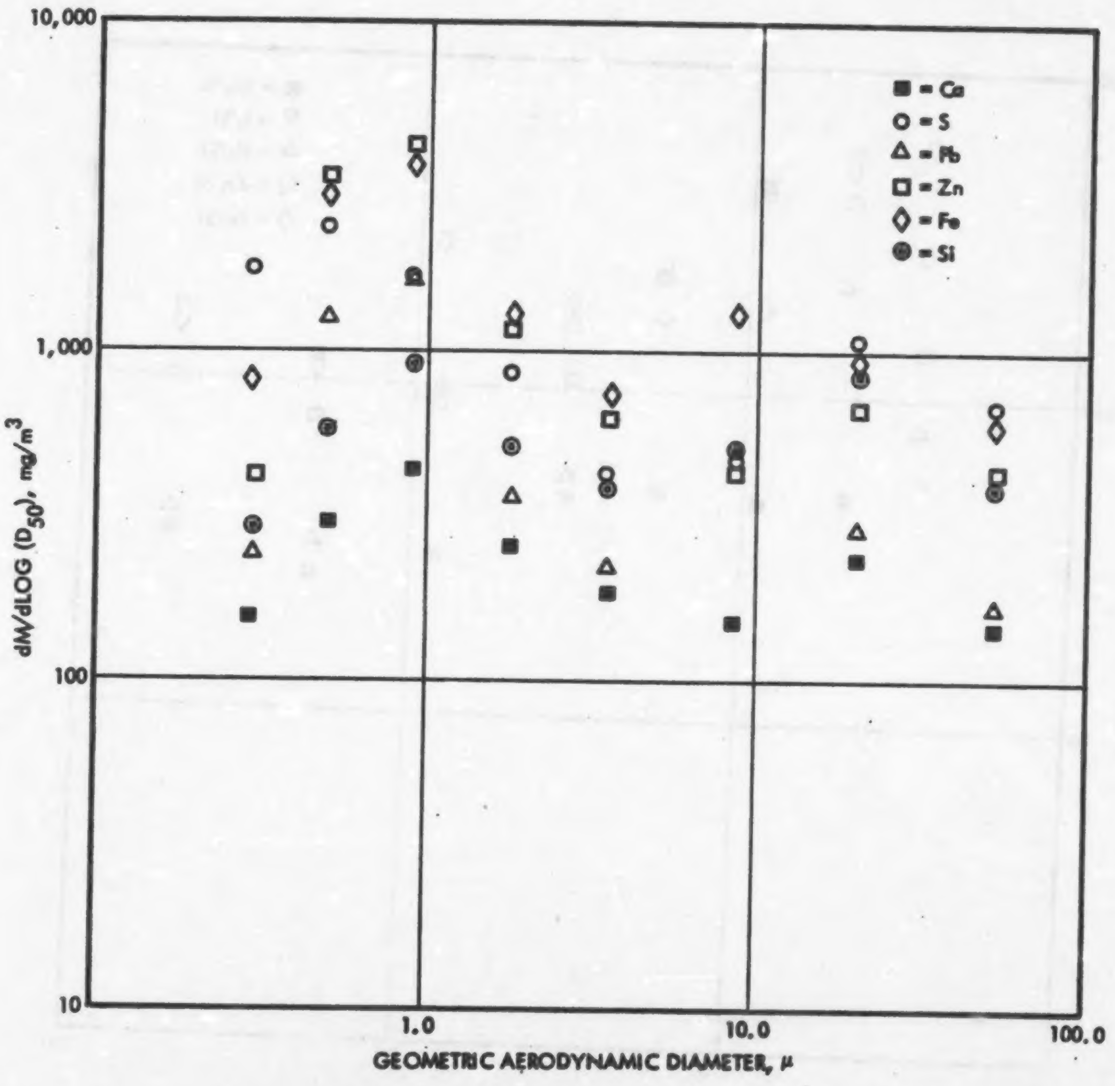


Figure 11. Trace Element Distribution by Particle Size at the Outlet of a Limestone Wet Scrubber

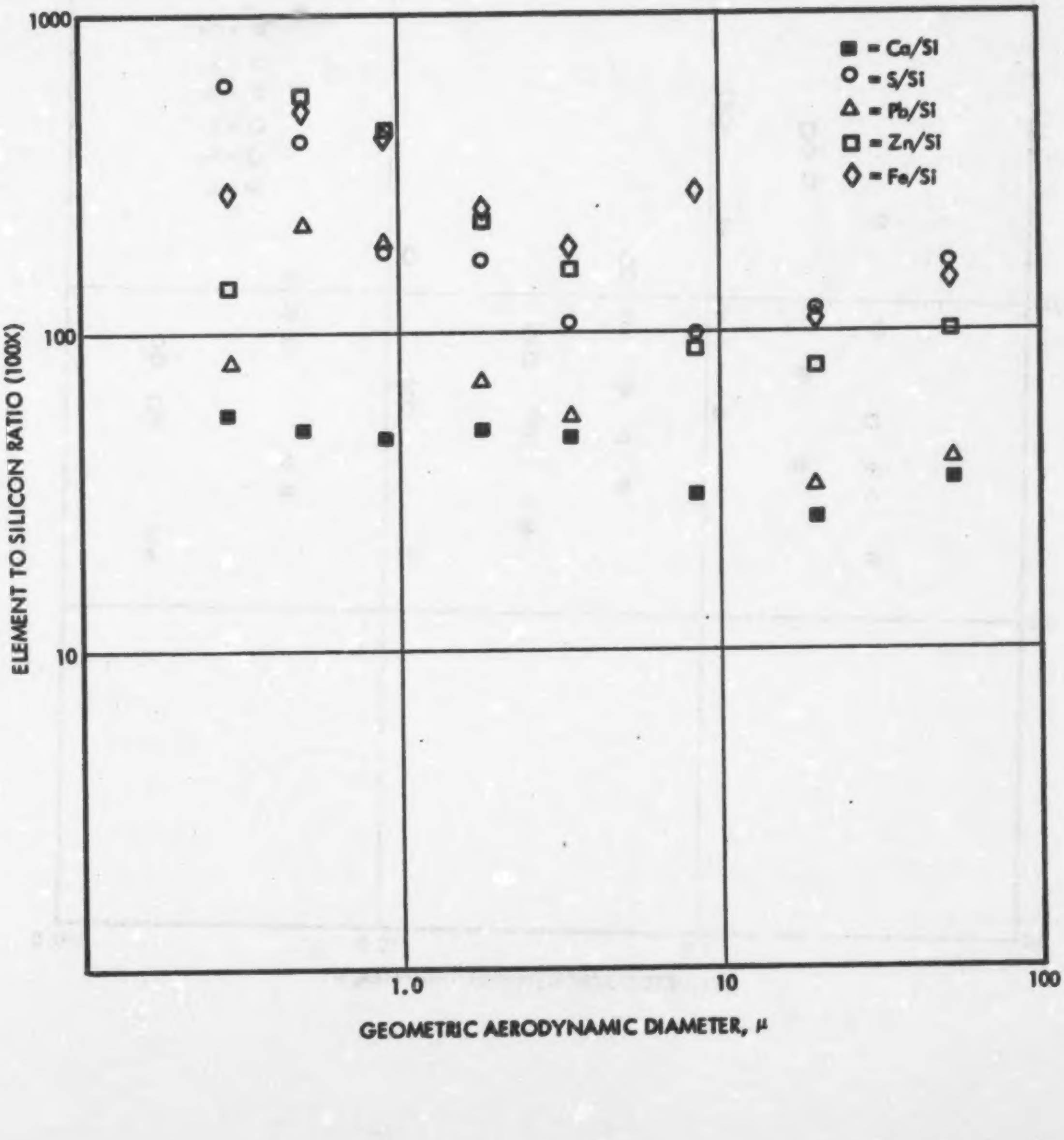


Figure 12. Ratio of Element Concentration to Silicon Concentration by Particle Size

the metals paralleling sulfur throughout impactor stages, but dropping off on the filter.

Results like these have been used to explain the reason for an apparent enrichment of certain elements after passage through a wet scrubber. Wet scrubbers as shown in Figure 9 emit mainly small particles and remove the large ones. If an element has a concentration increase with decreasing particle size, then preferential removal of the large particles would appear to make that element more concentrated in the outlet particulate matter. This hypothesis is illustrated by Zn which exhibited an enrichment across the scrubber and was found to have higher concentrations in the smaller particles.

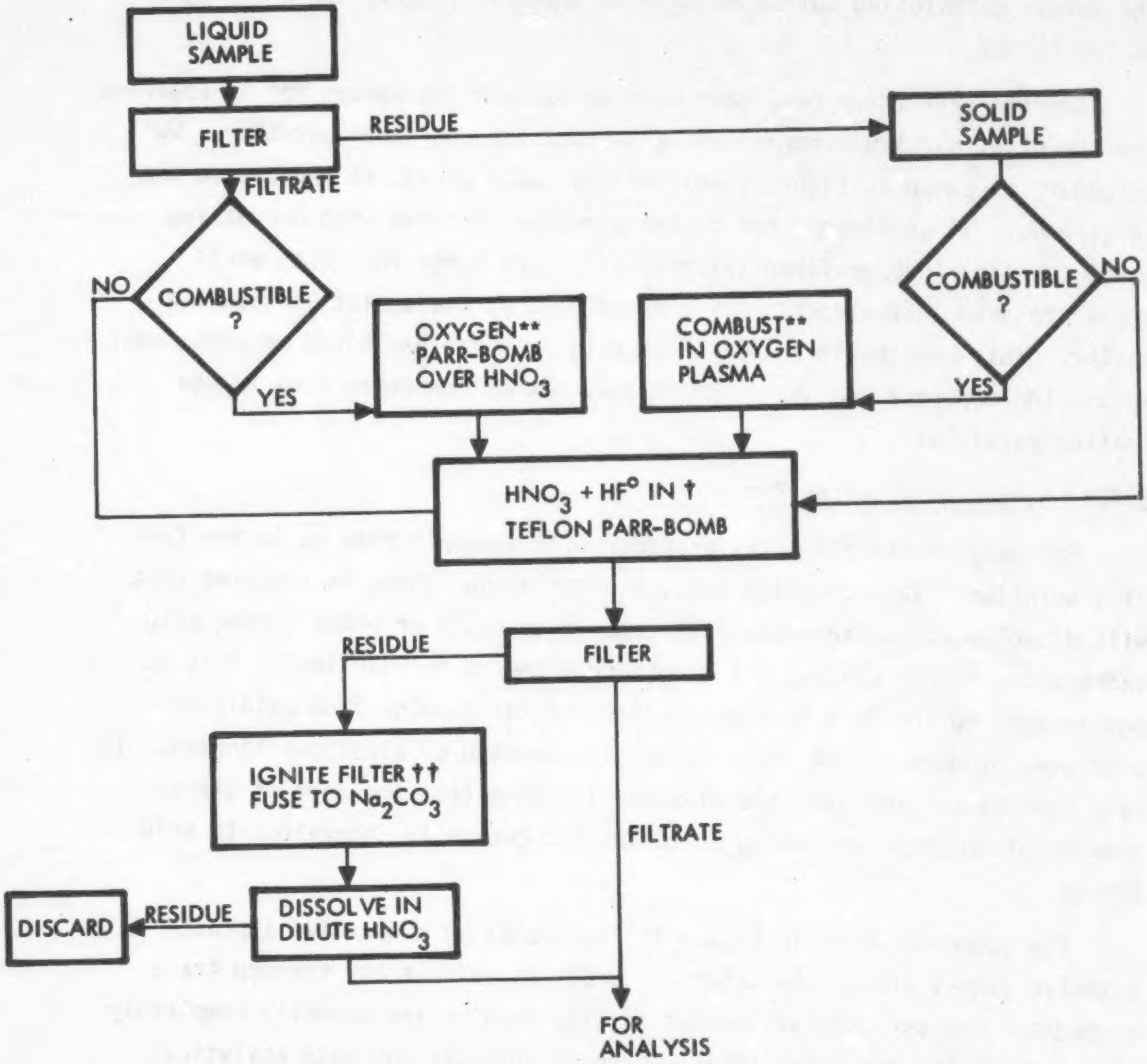
2.4.4 Sample Dissolution Procedures

For many of the elemental procedures, the sample must be in the form of a solution. To accomplish this, a dissolution scheme is required that will dissolve all of the material, since aqua regia or other strong acid extractions cannot release all the trace elements in solutions. This is due in part to the fact that most environmental samples from oxidizing processes produce an ash which is mostly composed of alumino-silicates. In many combustion processes the alumino-silicates take the form of glassy spheres which might be hollow or solid, but generally impervious to acid attack.

The approach shown in Figure 13 represents an exhaustive approach to dissolve almost all of the matrix in order to release any trapped trace elements. Fly ash samples treated in this fashion are normally completely dissolved in the HNO_3/HF solution which is suitable for most analytical methods. ICAP cannot tolerate HF due to the quartz capillary in the nebulizer, but the HF can be removed by heating with excess $HClO_4$. For additional information on dissolution schemes, see references 16 and 78.

2.5 SUMMARY OF INITIAL SAMPLE CHARACTERIZATION

Figure 14 presents the analysis flow for the initial sample characterization portion of the Level 2 inorganic compound identification scheme. As it was discussed in Section 1.0, the initial step is to evaluate the Level 1 SSMS data to determine which elements exceed their most toxic DMEG value. This step focuses the search on compounds which are potentially



* CATION ANALYSIS ONLY

† SILICON ANALYSIS NOT APPLICABLE

** PROBABLE LOSS OF SOME As, Se, Sb, Hg

†† SODIUM ANALYSIS NOT APPLICABLE IF THIS STEP PERFORMED (NOT NECESSARY IF ONLY LOOKING FOR Na)

° REMOVE HF PRIOR TO ICAP ANALYSIS BY HEATING WITH $HClO_4$ TO NEAR DRYNESS
(NOTE: LOSS OF As, Se, Sb, Hg POSSIBLE)

Figure 13. Flow Chart of Sample Dissolution Procedure

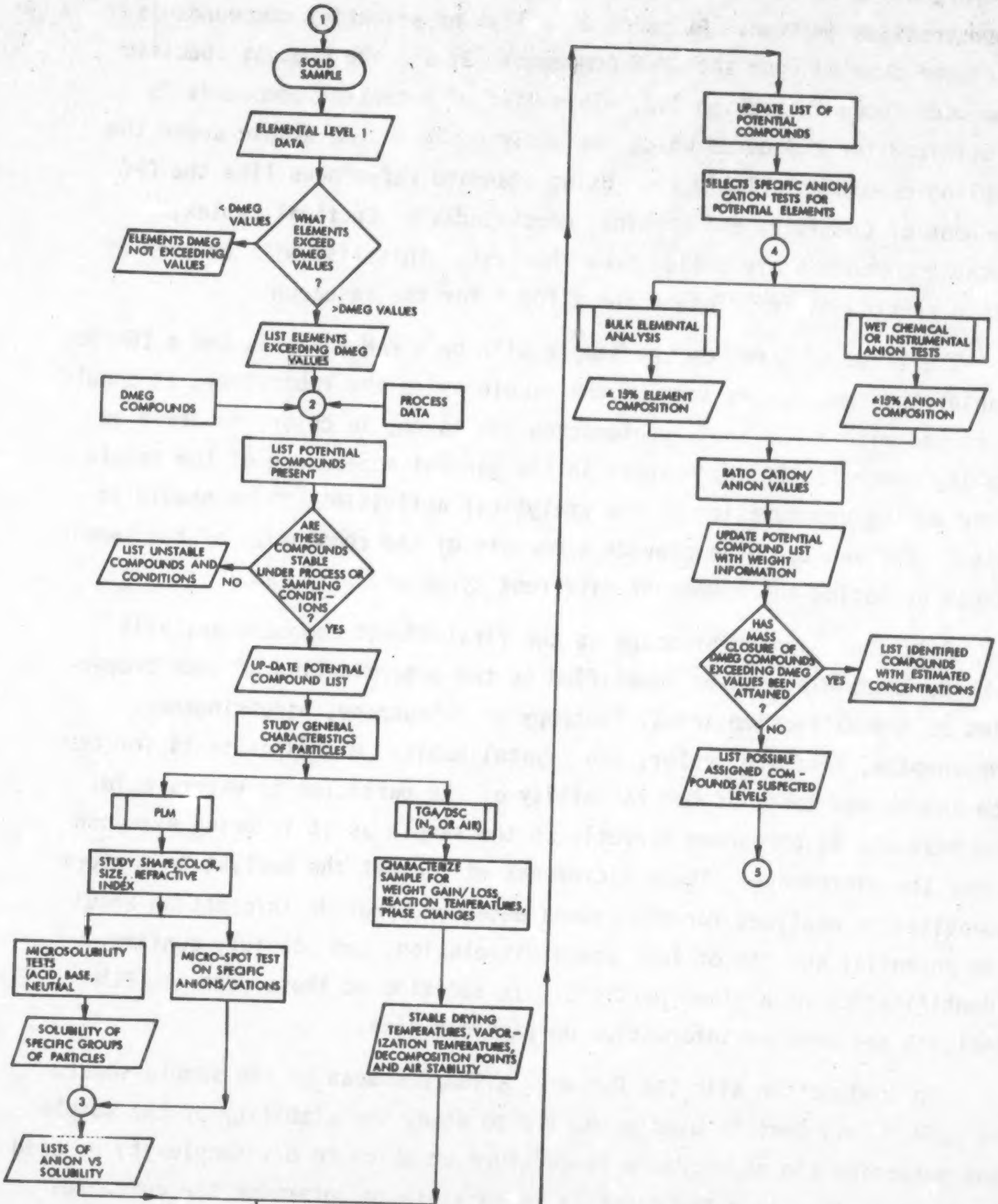

1
SOLID SAMPLE
ELEMENTAL LEVEL 1 DATA
WHAT ELEMENTS EXCEED DMEG VALUES ?
< DMEG VALUES
ELEMENTS DMEG NOT EXCEEDING VALUES
>DMEG VALUES
LIST ELEMENTS EXCEEDING DMEG VALUES
DMEG COMPOUNDS
2
PROCESS DATA
LIST POTENTIAL COMPOUNDS PRESENT
ARE THESE COMPOUNDS STABLE UNDER PROCESS OR SAMPLING CONDIT-IONS ?
NO
LIST UNSTABLE COMPOUNDS AND CONDITIONS
YES
UP-DATE POTENTIAL COMPOUND LIST
STUDY GENERAL CHARACTERISTICS OF PARTICLES
PLM
STUDY SHAPE COLOR, SIZE, REFRACTIVE INDEX
MICROSOLUBILITY TESTS (ACID, BASE, NEUTRAL
MICRO-SPOT TEST ON SPECIFIC ANIONS/CATIONS
SOLUBILITY OF SPECIFIC GROUPS OF PARTICLES
3
LISTS OF ANION VS SOLUBILITY
TGA/DSC (N_2 OR AIR)
CHARACTERIZE SAMPLE FOR WEIGHT GAIN/ LOSS, REACTION TEMPERATURES, PHASE CHANGES
STABLE DRYING TEMPERATURES, VAPORIZATION TEMPERATURES, DECOMPOSITION POINTS AND AIR STABILITY
UP-DATE LIST OF POTENTIAL COMPOUNDS
SELECTS SPECIFIC ANION/ CATION TESTS FOR POTENTIAL ELEMENTS
4
BULK ELEMENTAL ANALYSIS
WET CHEMICAL OR INSTRUMENTAL ANION TESTS
± 15% ELEMENT COMPOSITION
±15% ANION COMPOSITION
RATIO CATION/ ANION VALUES
UPDATE POTENTIAL COMPOUND LIST WITH WEIGHT INFORMATION
HAS MASS CLOSURE OF DMEG COMPOUNDS EXCEEDING DMEG VALUES BEEN ATTAINED ?
YES
LIST IDENTIFIED COMPOUNDS WITH ESTIMATED CONCENTRATIONS
NO
LIST POSSIBLE ASSIGNED COM-POUNDS AT SUSPECTED LEVELS
5

Figure 14. Logic Flow for Initial Sample Characterization

harmful, and eliminates those which probably are not harmful at the concentrations emitted. At point 2, a list of potential compounds is developed drawing upon the DMEG compounds (3) and the process specific compounds found in Section 1.2. This list of potential compounds is scrutinized for compounds which obviously could not be stable under the sampling conditions (Table 2). Using standard references like the CRC Handbook of Chemistry and Physics, Merck Index or Critical Tables, unstable compounds are culled from the list. This list will be used as both a checkpoint for closure and a focus for the research.

The first test run on the sample will be a PLM analysis and a TGA/DSC scan of the sample. As soon as the sample is in the laboratory, it should be viewed with a PLM and a photomicrograph taken, in color, to serve as quality control. If any changes in the general appearance of the sample occur during the duration of the analytical activities, these should be noted. The PLM can also provide a measure of the complexity of the sample simply by noting the number of different types of particles.

Polarized light microscopy is the first direct compound analysis method. Particles can be identified by the determination of such properties as the refractive index, isotropy or anisotropy, birefringence, pheochroism, fracture, color, and crystal habit. Microspot tests for common anions and tests of the solubility of the particles in water, acid, and base can be performed directly on the sample as it is being examined under the microscope. These microtests will alert the analyst to perform quantitative analyses for the anions detected, provide information about the potential success of full scale dissolution, and possibly confirm identification of a given particle. In addition to these data the PLM analysis can provide information on particle size.

In conjunction with the PLM work a TGA/DSC scan of the sample should be made. This test is used primarily to study the stability of the sample and determine the appropriate temperature at which to dry samples to be used in later tests. In a few cases it is possible to determine the compounds present by the weight loss at specific temperatures. At this point several of the major compounds will have been identified and the information on stability and morphology can be used to update the potential compound list.

By step 4 the analyst is ready to perform bulk elemental analysis and quantitative anion analysis on the samples. The elemental composition of the bulk sample may be determined by several techniques. Each has basic advantages and disadvantages which should be carefully weighed before chosing a particular method for analysis. ICAP is recommended for Level 2 analysis due to its low cost, acceptable sensitivity and its simultaneous multi-element analysis capability (up to 60 elements). Availability of instrumentation is a critical factor in chosing a method and therefore such methods as AAS, XRF and NAA might be used to supplement ICAP or be used in place of ICAP on the basis of availability. Whatever the choice, the instrument should be run in the most accurate fashion employing standards made up in the same matrix as the sample or using standard addition procedures to overcome any interferences due to the matrix. The goal is to achieve ±15% or better accuracy.

While an elemental analysis is being performed, anion analysis using an ion chromatograph (IC) will be performed. IC is recommended for anion analysis because of its ability to survey the sample qualitatively while quantitating most anions at the 1 ppm level. At the completion of anion and cation analysis the ionic charges (assuming the highest oxidation state) are compared and the degree of closure is assessed. Unless the PLM or TGA provided direct compound identification, it is possible only to say that some fraction of the cations is present as sulfates, chlorides, etc. In most combustion processes the remaining fraction can be assumed to be present as oxides.

At the end of the initial sample characterization, information will have been obtained in the following areas:

1. General appearance of a sample
2. Particle size distribution
3. Index of refraction and crystal structure
4. Weight loss with respect to temperature
5. Bulk elemental concentration
6. Bulk anion concentration

If this information is sufficient to narrow the possible choices of compounds to an acceptable level (based on the end use of the data), then the analyst may wish to stop. If there is a need for more specific compound identification, then this initial sample characterization will provide a strong starting point to interpret the data from the compound identification procedures discussed in the following section.

3.0 BULK CHARACTERIZATION

After initial sample characterization, bulk characterization begins. In this portion of the Level 2 analysis scheme the following techniques are applied:

- X-ray diffraction (XRD)
- Fourier transform infrared (FTIR)
- Electron spectroscopy for chemical analysis (ESCA) and Secondary Ion Mass Spectrometry (SIMS).

These techniques are described in Table 15 in summary form. The first phase of this Level 2 analysis scheme has taken a list of prospective compounds and compared them to the results from the elemental and anion tests. In addition some information from PLM on the compounds present will be available. With this as the starting point, an FTIR spectrum of the sample will be run. The IR spectrum will provide specific information on the functional groups present and possibly identify specific compounds. With this information in hand, interpretation of the XRD spectra will be greatly simplified. XRD provides direct compound information, but unfortunately it is normally sensitive only to materials present above ∿1% by weight. Finally depth profile analysis by ESCA or SIMS will be used to study the surface composition of the samples. Important information on the formation of trace element compounds can be gained as well as knowledge of surface reactivity or catalytic activity. This data is extremely important in predicting the toxicity of particles as they interact with lung tissue.

3.1 FOURIER TRANSFORM INFRARED ANALYSIS

Infrared spectroscopy has been widely employed in commercial and synthetic organic industries. The major strength of this technique is its applicability to both qualitative and quantitative analysis of most compounds in all phases (solids, liquids and gases). In general, infrared spectroscopy is fast, requires small quantities of sample, can differentiate between subtle compound structural differences, e.g., isomers, conformers, crystalline forms, and it can be applied to surfaces. Interpretation and quantitation of infrared spectra requires access to reference spectra,

Table 15. Summary Bulk Composition Characterization

Analysis Method	Principle of Operation	Information Derived	Compound Identification Procedure	Limitations
Infrared and Far Infrared	Many inorganic anions have specific absorption bands in infrared. These bands can be used to identify and quantify the anions present Either wet chemical or quantitative IR techniques directed toward specific anions	Used to determine presence of specific anions such as $MnO_4^{=}$, $PO_4^{\equiv}$, or $CrO_4^{=}$ Confirmation and quantitation of specific anions	Only small shifts are seen in the spectra with different cations. Anion information is essential for interpreting XRD data to eliminate potential compounds Ratio's of anion/cations used to predict potential compounds	Inorganic halogens have no bands in the IR Spectra can change depending on moisture content of sample Time consuming, since directed toward specific anion
Electron Spectroscopy for Chemical Analysis (ESCA)	Sample is irradiated with X-rays, causing inner shell electrons to be ejected: • Energy of these ejected electrons is a measure of the binding energy of electrons as modified by the chemical surroundings of the emitting atom • Energy shifts in the binding energy of electrons emitted from same element indicate different chemical environments	Elemental characterization determines oxidation state of elements present in sample Can determine bulk concentrations of homogeneous samples at or above 0.1% Though ESCA is extremely surface limited since electrons have shallow (3 to 20A°) escape depth, this makes the ESCA a very useful tool for studying absorption phenomena such as SO_2 on soot or flyash Most commercial instruments have ion (Ar+) beam for sequential removal of atomic layers for depth profile analysis	Direct compound identification not normally possible since there are usually only small shifts in binding energy of elements in the same oxidation state associated with anions or cations	Interpretation and quantitation of data is difficult and requires standards matching the matrix
X-Ray Powder Diffraction (XRD)	Powder sample diffracts a primary X-ray beam into a series of diffraction lines characteristic of a given crystalline substance Quantitative compound determinations are made, commonly using an internal standard with subsequent quantification by comparison to standard curves	Interpretation of diffraction pattern provides qualitative information on crystalline materials present. Diffraction lines are matched with spectra of pure compounds in the ASTM powder diffraction tables	The diffraction lines are studied and potential compound diffraction spectra are compared to lines in sample spectra Potential compounds are eliminated or proposed based on information from SSMS or AAS (elemental distribution), ESCA (oxidation state), and IR (anions present)	State of the art sensitivity is limited to ~0.05% depending on compound and matrix. Routine sensiture is closer to 0.5% Only crystalline materials can be seen

calibration with pure components and, most importantly, a knowledgable analyst.

Fourier Transform Infrared Spectroscopy (FTIR) obtains spectral information identical to that from conventional IR with the major advantage of greater sensitivity. The following sections will discuss the advantages of FTIR over conventional IR, sensitivities, principle of operation, available equipment, limitations, and implementation of FTIR to environmental samples.

3.1.1 Theory

Although the identical spectral information can be obtained from both conventional and Fourier Transformed Infrared Spectroscopy, it is obtained in quite a different manner. Conventional dispersive spectroscopy employs a prism or grating, which disperses the polychromatic infrared radiation into a spectrum of frequencies, and then scans the energy in each individual frequency interval sequentially. To obtain quality spectra with a dispersive instrument, narrow slits are required. The slits ensure that the frequency intervals, detected at any one time, are sufficiently narrow so that the desired resolution is obtained.

Interferometric spectroscopy, commonly called Fourier Transform Spectroscopy uses an interferometer instead of a grating or prism monochromator. The spectral information for all the frequencies is obtained at the same time during one scan whose duration is on the order of 1 sec. The actual spectrum is obtained by taking the inverse Fourier transform of the interferogram formed.

The most common interferometer used in Fourier Transform systems is the Michelson interferometer. (79) A simplified diagram of such an interferometer is shown in Figure 15. The interferometer consists of two mirrors at right angles to each other. One mirror is stationary while the other moves in a direction perpendicular to its front surface. A beamsplitter is positioned at an angle of 45 deg to the two mirrors, which divides the incident beam. Ideally, the beamsplitter should transmit 50% and reflect 50% of the light. The two beams pass to the stationary and moving mirrors and reflect to the beamsplitter. The beams are then recombined at the beamsplitter and exit the interferometer to the detector.

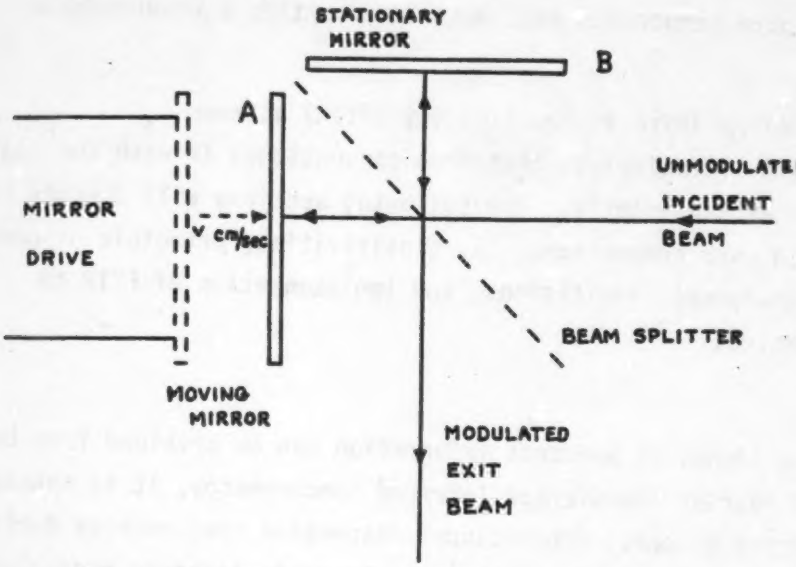


Figure 15. Diagram of Michelson Interferometer

Various degrees of interference (from totally constructive to totally destructive interference) are produced for each frequency by the optical path difference in the two arms. Consider a monochromatic source. When the optical path lengths of each arm of the two light beams are identical, there will be constructive interference of the two light beams when they recombine at the beam splitter. If the movable mirror is moved 1/4 of a wavelength, the two beams will be 180 deg out of phase when they recombine at the beam splitter; they will destructively interfere. Each individual incident frequency will produce an output oscillation with a cosine variation whose frequency is dependent on the incident frequency. Since each frequency can only interfere with itself, the output of the interferometer, the interferogram, for a polychromatic source is the sum of the oscillations at each individual frequency. The point of maximum intensity in the interferogram occurs at the position where the optical path lengths for the two arms of the interferometer are identical. It is only at this mirror position, that every frequency constructively interferes. Thus, it can be seen that the interferometer establishes specific phase relationships for each frequency as a function of mirror displacement. The resultant interferogram is related to the intensity as a function of frequency spectrum by a Fourier transformation. Fourier analysis of the interferogram picks out the pattern for each frequency and determines the magnitude of the oscillation at that frequency, the Fourier coefficient. The Fourier Transform analysis is a tedious process and must be handled by high speed computers.

Commercial Fourier spectrometers are based mostly on the Michelson interferometer. They differ little in principle, but vary greatly as far as the optical, mechanical and electronic components are concerned. The spectral ranges covered depend on the nature of the beam splitter and detector. Most instruments cover the range from 40,000 cm^{-1} to 10 cm^{-1} (0.25 to 1000 microns) with scan times from about 1/10th second to several hours. Computer capabilities are present on all marketed instruments.

3.1.2 Advantages of FTIR

Fourier Transform spectroscopy is a less direct way of obtaining a spectrum than conventional dispersive spectroscopy; however, there are certain advantages that make the interferometric method favored over the dispersive method. The most important points are:

- The increased energy throughput (Jacquinot's advantage) - There are no slits and throughput is limited by the size of the mirrors, 100 to 200 times better than a dispersive instrument. (80,81)
- The multiplex advantage (Fellgett's advantage) - The interferometer receives information from all frequencies in the spectrum simultaneously and therefore, the signal for each resolution element is proportional to T, where T is the total scan time. For equivalent scanning times and optical throughput, the rapid interferometer has a higher signal-to-noise ratio than conventional IR. The signal-to-noise ratio can be improved proportionately to the number of scans. (81,82)
- The improved accuracy of the frequency scale - The position of the movable mirror is controlled by a reference interferometer that has a monochromatic laser as a light source. This internally calibrates the frequency scale and is not sensitive to the system's temperature or humidity. (83)
- The computer capabilities - The inverse Fourier transform of the interferogram must be computed to obtain the intensity as a function of frequency spectrum. The utilization of the fast Fourier transform algorithm of Coley and Tuckey (84) by a dedicated minicomputer makes on-line Fourier analysis a reality. Digitized spectral data are produced by this process and once a spectrum is recorded and stored, the computer can aid in data presentation, enhancement and interpretation.

Simply, the FTIR has increased sensitivity, increased speed, and better wavelength accuracy than conventional IR with computer capabilities for data reduction.

3.1.3 Application of FTIR to Environmental Samples

Environmental particulate samples undergoing infrared analysis truly require the advantages attained from both Fellgett's and Jacquinot's principles. These samples generally are poor infrared energy transmitters and the compounds of interest to the Level 2 analysts can be present at concentrations less than 1%.

When applying FTIR to characterize environmental samples, the analyst should be aware that:

- The identification of inorganic compounds by infrared spectroscopy is nonroutine. There is not a wealth of reference spectra to aid the analyst in interpretation.
- Although FTIR is a rapid analytical method, the complexity of environmental samples warrants careful and labor intensive sample preparation. Representative samples must be acquired once optimum sample quantities and drying temperatures are determined and compound verification and quantitation is best accomplished by standard addition techniques.
- Many simple inorganic compounds such as borides, silicides, nitrides and oxides, do not absorb radiation in the region between 4000 and 600 cm^{-1}. Therefore, the far-infrared region, 200 to 10 cm^{-1}, must be scanned. This necessitates that many solids be prepared twice for FTIR using two dispersing agents for optimum spectra definition.
- The identification of polyatomic anions, e.g. $CO_3^{=}$, $SO_4^{=}$, NO_3^{-}, etc., is straightforward. However, compounds such as KNO_3 can be distinguished from $NaNO_3$ or $Ca(NO_3)_2$ only when standard spectra are available. In this case elemental data obtained from the initial sample characterization can be used to decide which compound is present.
- Inorganic compounds can react with many of the standard IR window and support materials (cation exchange). The analyst must be aware of this and decide on the most stable paraparative medium.

Inorganic compound identification of environmental samples has been successfully employed (85,86) in characterizing samples from a Fluidized Bed Combustor (FBC).

The sample types considered in this discussion are loose particulates (cyclone catches, bulk solids, e.g. feed materials, slurry solids, overflow bed materials, ash, waste solids, etc.), filters (SASS train, water filtrates, etc.), and MRI impactor stages (Kapton lines and neat). FTIR can be successfully employed in the analysis of gaseous grab samples for many inorganic gases, e.g., CO, CO_2, NH_3, NO_2, SO_2, $Ni(CO)_4$, AsH_3, or PH_3. (87,88)

The moisture content of a sample affects the spectral quality and in many cases drying is necessary to produce well resolved spectra. Information from TGA analysis should be used by the analyst to establish a drying temperature which allows water evaporation without sample decomposition. FTIR scans should be run, if time and sample quantities are sufficient, both with and without drying.

Recommended sample preparation methods for the various sample types considered in this manual are given in Table 16. Although other mulling agents and window materials are available, those recommended are free from ion exchange reactions. (89) In the mulling technique, finely ground particulates (<40 micron grain size) are suspended in the mulling agent and the resultant slurry is supported between two infrared transmitting windows.

Table 16. Recommended FTIR Sample Preparation Techniques

Sample Type	Spectral Region	Mulling Agent	Window Material	Comments
Loose Particulates and MRI Stages*	3800-1333 cm^{-1}	Fluorolube	BaF_2	These window combinations provides good quality spectra without ion exchange reactions
	1333- 400 cm^{-1}	Nujol	AgCl	
	600- 45 cm^{-1}	Nujol	Polyethylene	
Filters	3800- 45 cm^{-1}	None	KRS-5	Attenuated Total Reflectance (ATR)

*After removal with distilled in glass or spectro-grade hexane and room temperature evaporation.

Most samples do not require prolonged grinding and adequate dispersions are obtained from a 10% (e.g. 25 mg sample/250 mg mulling agent) sample loading. Hand grinding in an agate mortar and pestle produces well ground samples for most environmental particulates. Additional sample or mulling agent can then be added until a spectrum of desired intensity is obtained. Teflon, aluminum, or polyethylene standard spacers can be used to control path length for samples undergoing species quantitation or to obtain more intense scans. The computer capabilities available in FTIR do not necessitate strict control of path length for quantitation as data can be ratioed to the intensities of the mulling agent absorption peaks. However, control of path length is sometimes necessary to obtain high quality spectra.

An example of an acceptable quality spectrum is shown in Figure 16 (44). This spectrum was taken of particulate matter emitted from an FBC. The expected material ($CaSO_4$, $CaCO_3$, SiO_2) is clearly visible. These particulate samples were hand ground, mulled with Nujol (mineral oil) and supported on AgCl windows. Forty scans were averaged in this test, although more scans could have been made if higher sensitivity were warranted. In most cases, the performing analyst's judgement determines the parameters for instrumental operation. The analyst observes the obtained spectrum and determines: which spectral regions require more scans for improved sensitivity, which wavelength regions require better point-to-point resolution for ease of interpretation, and what computer data manipulations (e.g., subtraction of mulling agent and window backgrounds, comparison with standards, comparison with other samples, quantitation) are essential.

The application of Level 2 inorganic analytical techniques to samples before and after aqueous and acid extractions (leachate studies) provides important environmental toxicity information:

- Surface compounds are removed and interior ones exposed for identification.
- Waste storage and ground water pollutant potential is evaluated.
- The impact on throat and lung tissue, which readily absorb water extractable compounds, is characterized.

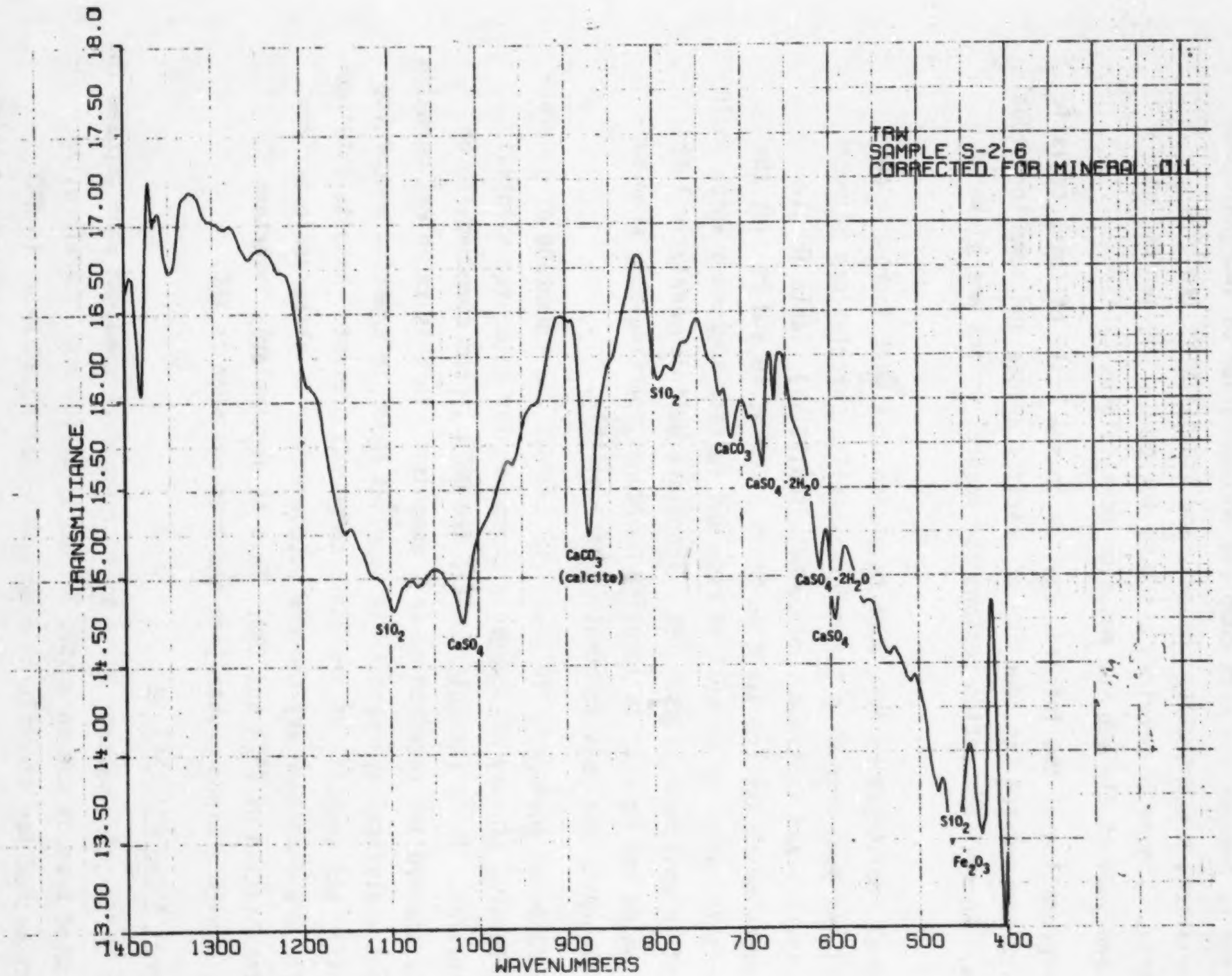


Figure 16. FTIR of Outlet FBC Material

FTIR's computer capability for digital wavelength subcontraction is technically suited to provide the most complete documentation of inorganic compounds' behavior, concentration changes, and stability in leaching environments. Figure 17 provides a scheme for conducting surface and leachate analysis of fly ash and emission particulates by FTIR.

Interpretation of the infrared spectra on the basis of characteristic frequencies can provide the identity of specific anions and some individual compounds. General absorption regions for several anions are given in Table 17.

Several investigators have done extensive work with inorganic compounds (9) and have been able to produce specific correlations between observed spectra and individual compounds. (89,90,91) Table 18 gives a general overview of the inorganic IR bands. Tables 19 and 20 list the characteristic bands for several nitrate and sulfate compounds which could be present in environmental samples. There are definite analytical frequencies which can be used to identify compounds, particularly when supporting elemental analysis information is available.

The computer equipped FTIR gives the analyst the advantage of generating an extensive library of inorganic compounds for automated spectral interpretation. It is feasible for all the DMEG listed compounds to be prepared, scanned and retained on this computer. In this technical manual's integrated analytical approach, FTIR supplies major information concerning the identify and quantity of inorganic compounds present. Results obtained using FTIR are complementary and are supplementary to those achieved from the implementation of ESCA and XRD. This is particularly important for materials which are non-crystalline and thus not seen in XRD.

3.2 Powder X-ray Diffraction

The diffraction pattern given by a crystalline compound when exposed to a collimated beam of monochromatic X-rays is unique and, therefore, an excellent method for identifying compounds. Recent advances in XRD instrumentation and procedures have improved compound detection sensitivity to 0.05% (92,93). Compound selectivity and improved sensitivity make XRD a necessary analytical technique for Level 2 inorganic compound identification. This section discusses the principle of operation, available

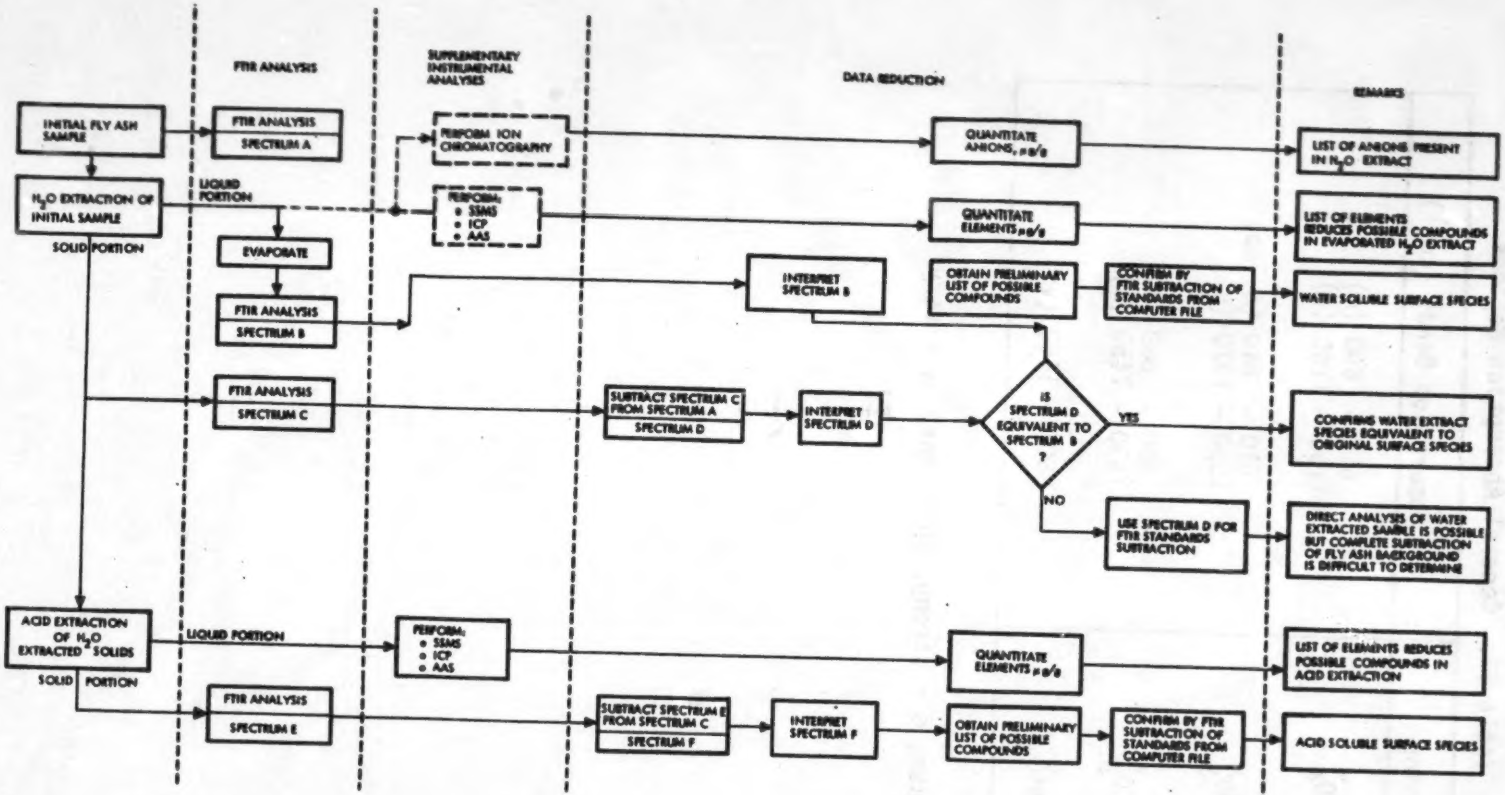

FTIR ANALYSIS
SUPPLEMENTARY INSTRUMENTAL ANALYSES
DATA REDUCTION
REMARKS
INITIAL FLY ASH SAMPLE
FTIR ANALYSIS
SPECTRUM A
PERFORM ION CHROMATOGRAPHY
QUANTITATE ANIONS, μg/g
LIST OF ANIONS PRESENT IN H_2O EXTRACT
H_2O EXTRACTION OF INITIAL SAMPLE
LIQUID PORTION
PERFORM:
• SSMS
• ICP
• AAS
QUANTITATE ELEMENTS μg/g
LIST OF ELEMENTS REDUCES POSSIBLE COMPOUNDS IN EVAPORATED H_2O EXTRACT
SOLID PORTION
EVAPORATE
FTIR ANALYSIS
SPECTRUM B
INTERPRET SPECTRUM B
OBTAIN PRELIMINARY LIST OF POSSIBLE COMPOUNDS
CONFIRM BY FTIR SUBTRACTION OF STANDARDS FROM COMPUTER FILE
WATER SOLUBLE SURFACE SPECIES
FTIR ANALYSIS
SPECTRUM C
SUBTRACT SPECTRUM C FROM SPECTRUM A
SPECTRUM D
INTERPRET SPECTRUM D
IS SPECTRUM D EQUIVALENT TO SPECTRUM B ?
YES
CONFIRMS WATER EXTRACT SPECIES EQUIVALENT TO ORIGINAL SURFACE SPECIES
NO
USE SPECTRUM D FOR FTIR STANDARDS SUBTRACTION
DIRECT ANALYSIS OF WATER EXTRACTED SAMPLE IS POSSIBLE BUT COMPLETE SUBTRACTION OF FLY ASH BACKGROUND IS DIFFICULT TO DETERMINE
ACID EXTRACTION OF H_2O EXTRACTED SOLIDS
LIQUID PORTION
PERFORM:
• SSMS
• ICP
• AAS
QUANTITATE ELEMENTS μg/g
LIST OF ELEMENTS REDUCES POSSIBLE COMPOUNDS IN ACID EXTRACTION
SOLID PORTION
FTIR ANALYSIS
SPECTRUM E
SUBTRACT SPECTRUM E FROM SPECTRUM C
SPECTRUM F
INTERPRET SPECTRUM F
OBTAIN PRELIMINARY LIST OF POSSIBLE COMPOUNDS
CONFIRM BY FTIR SUBTRACTION OF STANDARDS FROM COMPUTER FILE
ACID SOLUBLE SURFACE SPECIES

Figure 17. FTIR Analysis of Surface Composition of Fly Ash Samples

Table 17. General Absorption Regions

Anion	Absorption Bands (cm^{-1})
$SO_4^=$	610 - 690 (m) 1130 - 1180 (s)
NO_3^-	610 - 640 (m, sp) 1350 - 1370 (s)
$CO_3^=$	650 - 680 (m) 1430 - 1450 (s)
$SiO_3^=$	~900 - 1100 (vs)

m = medium, s = strong, sp = sharp, v = very

Table 18. Listing of Assigned Infrared Bands Observed in Particulate Samples

Frequency, cm^{-1}	Species	Frequency, cm^{-1}	Species
3140	NH_4^+	1120	PO_4^{3-}
3020	NH_4^+	1110	SO_4^{2-}
2920	HYDROCARBON (C-H)	1035	SiO_4^{4-}
2860	HYDROCARBON (C-H)	980	SO_4^{2-}
2800	NH_4^+	880	CO_3^{2-}
1768	NO_2^-(BULK)	840	NO_3^-(BULK)
1720	NH_4^+ (HALIDE)	800	SiO_4^{4-}
1620	H_2O	780	SiO_4^{4-}
1435	CO_3^{2-}	728	CO_3^{2-}
1400	NH_4^+	670	PO_4^{3-}
1384	NO_3^- (SURFACE)	627	PO_4^{3-}
1360	NO_3^- (BULK)	620	SO_4^{2-}
1190	PO_4^{3-}	600	PO_4^{3-}
1140	PO_4^{3-}	470	SiO_4^{4-}

Table 19. Infrared Bands of Some Common Nitrates (cm^{-1})

Compound	Band Category(a)				
	VW	W	M	S	VS
$NaNO_3$	2428		836 sp		1358 1790
KNO_3			824 sp		1380 1767
$Ca(NO_3)_2 \cdot XH_2O$	1044		820 sp	~1430 ~1640	~1350
$Fe(NO_3)_3 \cdot 9H_2O$			835 sp	1615	1361 ~1785
$Ca(NO_3)_2 \cdot 3H_2O$	2431		836 sp	1587	1378 1790
$Pb(NO_3)_2$		807	726 836 sp		1373

W = Weak, M = Medium, S = Strong, V = Very, SP = Sharp, B = Broad

Table 20. Infrared Bands of Some Common Sulfates (cm^{-1})

Compound	Band Category[(a)]				
	VW	W	M	S	VS
Na_2SO_4		645		620	1110
K_2SO_4					1110 620
$CaSO_4 \cdot 2H_2O$		1010 (sh) 1670	318 2200 (b)	603 667 1630 (sp) 3410 (b)	1130 (vb)
$MnSO_4 \cdot 2H_2O$		510 (vb) 607	660 1025	825 3225 (b)	1135 (vb)
$FeSO_4 \cdot 7H_2O$	990	1150 (sh)	1625	611 (vb) 3330 (b)	1090 (vb)
$CuSO_4$		1020 (sp) 1600 (sh)	680 805 860	1200 ~3300 (b)	1090 (vb)
$PbSO_4$			592 (sp) 623 (sp)		

(a) V = Very, W = Weak, M = Medium, S = Strong, SH = shoulder, B = Broad, SP = sharp equipment, advantages, limitations, and application of powder X-ray diffraction analysis to environmental samples.

3.2.1 Theory

The atoms that make up a crystal or crystalline material occupy a three-dimensional periodic array. The arrays of atoms in the crystal make up planes which diffract the X-rays in much the same way as a grating diffracts ordinary light. The relationship between the X-ray wavelength, λ, the angle between the incident and diffracted beam, Θ, and the interplanar distance in the crystal, d, is found in the Bragg equation, shown below:

$$n\lambda = 2d \sin \Theta \qquad (1)$$

where n is the order of the diffraction. If the x-ray beam is monochromatic, there will only be a limited number of angles at which constructive diffraction of the beam will occur.(94)

In the case of a single crystal, the diffraction will consist of a series of individual diffracted beams arranged systematically according to the symmetry of the crystal and the manner in which it is oriented. If very many small, randomly oriented crystals are placed in the X-ray beam, each Bragg reflection will consist of a continuous cone of diffracted rays. Any specific crystalline material will produce a series of cones of fixed angle and fixed relative intensity. The intensity of the diffracted ray is dependent on the kind of atoms and their arrangement in the "unit cell," which is the smallest repeating unit in the crystal. Thus, any one particular crystalline compound can be identified from its X-ray pattern which is distinguished by a unique set of d spacings and intensities.

Two basic types of instrumentations are used to detect diffracted X-rays: 1) film, and 2) Geiger or scintillation counters. Camera units are advantageously used when: (1) the quantity of material available for analysis is small, as determinations can be made on as little as 2 ng, or (2) when the sample is reactive or volatile. In both cases the sample is sealed within a glass capillary tube filled to <1 cm in to depth.

By knowing the wavelength of the incident X-ray, the d spacings of the planes in the crystal can be determined by measuring the film, and calculating the Bragg angle. Suitable tables are available to simplify this procedure. (95) This method of examining powders is called the Debye-Scherrer-Hull method, or the powder diffraction method. X-ray diffraction units employing Geiger or scintillation counters require larger sample sizes of 50 to 100 mg of material. For environmental samples, the Geiger or scintillation detectors are generally used, since more accurate line resolution and intensities are obtained from the strip chart recorder or the computer printout. An ancillary piece of equipment which has been effectively used with Geiger or scintillation detectors is a graphite monochromator. This attachment, mounted between the sample compartment and the detector assembly, isolates the incident X-ray wavelength of interest from background radiation. This has the effect of improving the sensitivity from ∿ 1-2% of material present to 0.1 - 0.3%. (93)

The application of XRD to environmental samples has two major limitations: (1) small amounts of the pure compounds of environmental interest, <0.1%, are usually mixed with an amorphous matrix and (2) the glass fiber filters used in particulate sampling systems produces a background scattering which can mask the diffraction pattern due to crystalline species. These application difficulties can be minimized through the use of the instrument operating and sample handling procedures given in the following section.

3.2.2 Powder XRD For Compound Identification in Environmental Samples

An XRD unit employing a Geiger or scintillation counter and a graphite monochromator is recommended for the analysis of environmental samples of loose particulate matter and particles impacted on glass fiber filters.

Sample mounting (93) to take advantage of strong diffractions at low angles for some compounds requires that the sample be spread in a thin film over the illuminated area. Filter samples can simply be cut into 2.5 cm x 7.5 cm strips and mounted on glass microscope slides using double sided adhesive tape.

Loose particulate matter must first be ground to <40μ in an agate mortar and pestle. Care should be taken to avoid excessive force which might cause sufficient localized heating to alter the sample's chemical make-up. Fifty to one hundred mg of the ground sample is then ultrasonically dispersed in 1 to 2 ml of a 1:4 mixture of collodion in alcohol.

The mounting plate is a microscope slide which has been covered with double-sided adhesive tape. An area of 15 mm x 35 mm is masked off with masking tape to form a shallow trough. The collodion suspension is poured into this trough and carefully spread until an even, thin film is formed in the trough. After the slide dries, it is ready for analysis. This mounting scheme using the double side adhesive type has reduced the problems (96) of cracking and buckling of prepared samples. Care still should be taken to avoid undue handling and excessive humidity or temperature changes.

Another mounting technique adds the ground particulate matter to amyl acetate to form a slurry. This slurry can then be poured into the masked off area on the microscope slide. Once the amyl acetate is allowed to evaporate, the sample is ready for analysis. Finally, a thin layer of petroleum jelly could be spread over the surface of the microscope slide. The loose particulate matter can then be sprinkled over the greased area.

After obtaining the XRD spectrum, the resultant data is converted into d-spacings in Angstrom (Å) units and relative intensities. This data is then used in searching the ASTM Powder Diffraction file to identify compounds present. Due to the complex nature of the majority of environmental diffraction spectra, it is also advantageous to have available the results of preliminary survey analysis for major elements and anions to reduce the number of possible compounds. In addition the potential compound list can be used as a starting point to search the ASTM file. Identification of a compound is considered valid if the primary and secondary diffraction lines are found with less than ±0.0.5 Å differences.

Quantitative analysis is best accomplished using standards prepared in silicic acid matrix, to produce the type of amorphous background present in fly ash. Standards can also be produced from compound additions to NBS fly ash or a standard addition technique to the sample undergoing analysis. Glassfiber filters present a challenge to developing standards, since particles can penetrate the filter forming a non-homogeneous dispersion in the glassfilm. One way to surmount this problem is to place the standards on a glassfiber filter. The apparatus to do that is shown in Figure 18. It consists of a large (~1L) wide mouth jar, wide enough to accept 7.5 cm open face filterholder and two or more tapered tubes arranged around the filter. A ground (<40μm) sample of the standard (or standards) is placed on the bottom of the jar at the focus of the nozzles.

After the filterholder is loaded with a pre-weighed glassfiber filter, and connected to the vacuum pump, the pump is turned on and sufficient flow is maintained to suspend the sample. After a fixed period of time the filter is removed, weighed, and the surface loading calculated. Additional standards at different surface loadings are made by varying the pumping time.

Using these techniques TRW has found a variety of inorganic compounds. In all the environmental samples analyzed numerous diffraction lines were obtained and XRD pattern interpretation was complicated but rewarding. Major compounds (>1%) were readily identified, many minor ones, <1%, identified and quantitated, and detection limits were established for inorganics of environmental interest in the process streams. Table 21 tabulates the detection limits for several compounds of environmental interest (found by experiment).

The application of powder XRD to environmental assessment samples will continue to produce a usable data base for future inorganic compound identification efforts.

Table 21. Detection Limits on Commercial XRD Instruments for Several Compounds

Compound	Estimated Detection Limit (%W/W)
$CaSO_4$	~1
As_2O_3	2
$HgSO_4$	~2
PbO	≤1
Cr_2O_3	~3-5
MnO_2	~2

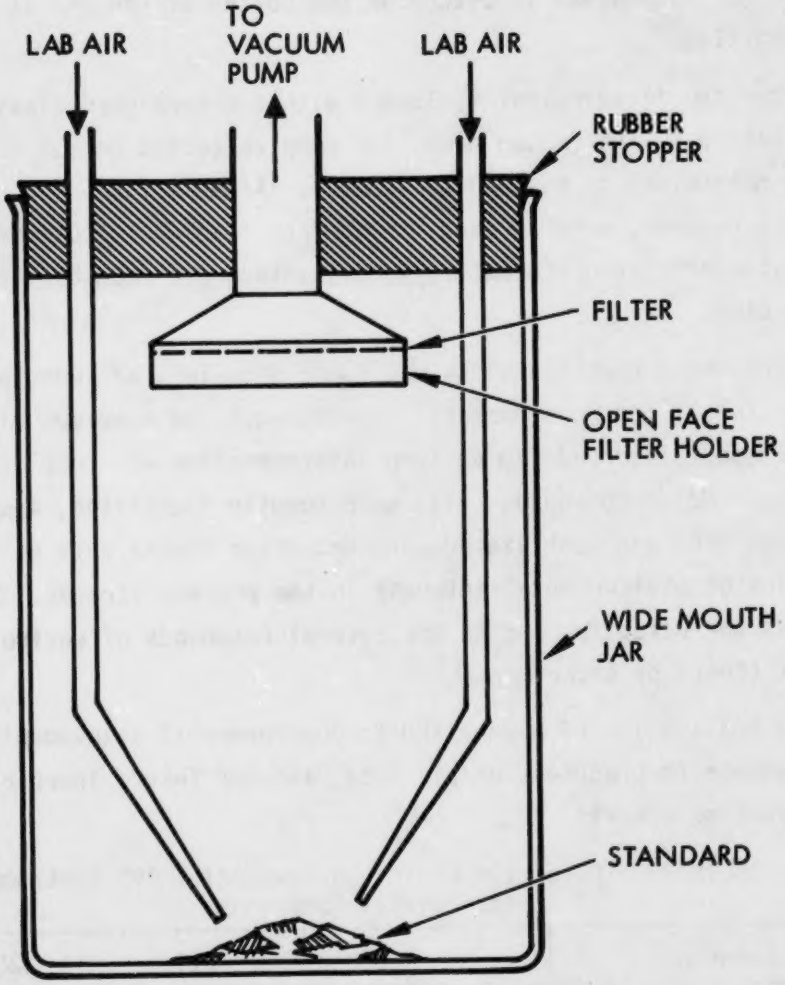


Figure 18. Powder Dispersing Apparatus For Preparing XRD Standards on Glassfiber Filters

3.3 SURFACE ANALYSIS USING ESCA AND SIMS

One facet of the bulk characterization of environmental samples is the study of the surface composition. Obviously those materials that are present on the surface will be the first to be released into the environment. The surface can be involved in catalysis and chemical reactions in the atmosphere, toxic affects in the lung, or leaching of trace elements in a landfill. For these reasons an understanding of the surface composition of a particle will be important to assess the environmental impact of particulate matter emissions. The following sections describe the use of X-ray Photoelectron Spectroscopy (XPS or its more common name ESCA for Electron Spectroscopy for Chemical Analysis) and Secondary Ion Mass Spectrometry (SIMS) for surface analysis.

3.3.1 Theory

This section will relate some of the key concepts in ESCA and SIMS so that an environmental chemist can understand and use the data obtainable from ESCA or SIMS. Several good survey articles on ESCA are available, (98, 99, 100, 101) but for an extensive review of the theory of ESCA the reader is directed to Siegbahn's work. (102) A good series of articles on SIMS is contained in Heinrich. (103) For a general survey on SIMS and surface analysis, the two articles by Evans (104, 105) are recommended.

Fundamentals - ESCA - An ESCA spectrum results when a beam of monoenergic X-ray photons ($h\nu$) is directed at a sample. The X-rays are absorbed by the sample's atoms and result in the emission of an electron. The kinetic energy (E_k) of the emitted electron plus the energy required to remove it from the atom (binding energy) must equal the energy of the X-ray photon. In practice an additional energy correction is required for the work function (ϕ) of the spectrometer material. Thus, the binding energy (E_b) can be determined from:

$$E_b = h\nu - E_k - \phi$$

While all electrons with binding energies less than the X-ray photon can be ejected, not all electrons have the same probability of being ejected. Consequently, the intensity of an ESCA signal for a given atom will vary depending on the orbital of the electron's origin. Figure 19 shows an example of the survey spectrum obtained from an FBC particulate matter sample. Any element above H can be detected; in this example, Ca, O, C, Si, Al, and Fe were found. Table 22 compiled from Siegbahn (102) and Beardon(106) lists the principle ESCA lines by element. The reason that ESCA is a surface technique is that the mean free path (MFP) for an electron in a solid is limited. The source X-rays penetrate deeply into the sample, but only those electrons ejected from near the surface escape to be analyzed. The remainder suffer energy losses and appear as background radiation. The MFP of an electron is dependent on its kinetic energy and the matrix. At the present time some rule of thumb estimates for MFP are: 5-20Å in metals, 15-40Å in oxides, and 40-100Å in polymers. (107, 108)

Depth profile analysis is possible by employing an Ar^+ beam to remove layers of the sample. The sputter rate will depend greatly on the matrix, so that for highly accurate results standards are essential. Standards should be made so that an Ar^+ beam operating at standard conditions can be calibrated for its sputter rate in a given matrix. For ash samples no procedure has been developed to calibrate beam sputter rates, but most instrument manufacturers have information on other silicate matrices which can be applied to fly ash. Unless quantitative measurements on surface concentration are going to be made, qualitative estimates of the sputter depth will be sufficient to characterize the sample.

Fundamentals - SIMS - Secondary Ion Mass Spectrometry is the general name applied to techniques which use a beam of primary ions to produce ions from the surface for mass analysis. The diameter of the beam used to sputter the ions from the surface can be spread over several millimeters of sample, or focused into a narrow beam (2-300 μm). The latter systems are normally called Ion Microprobe Mass Analyzer (IMMA) to discriminate their ability to provide depth and high lateral resolution of the elemental composition of the surface analyzed. For the most part, this discussion will be directed at IMMA units, since they can be operated in either a focused (<1 μm resolution) or rastered mode to provide survey composition information over a wide area.

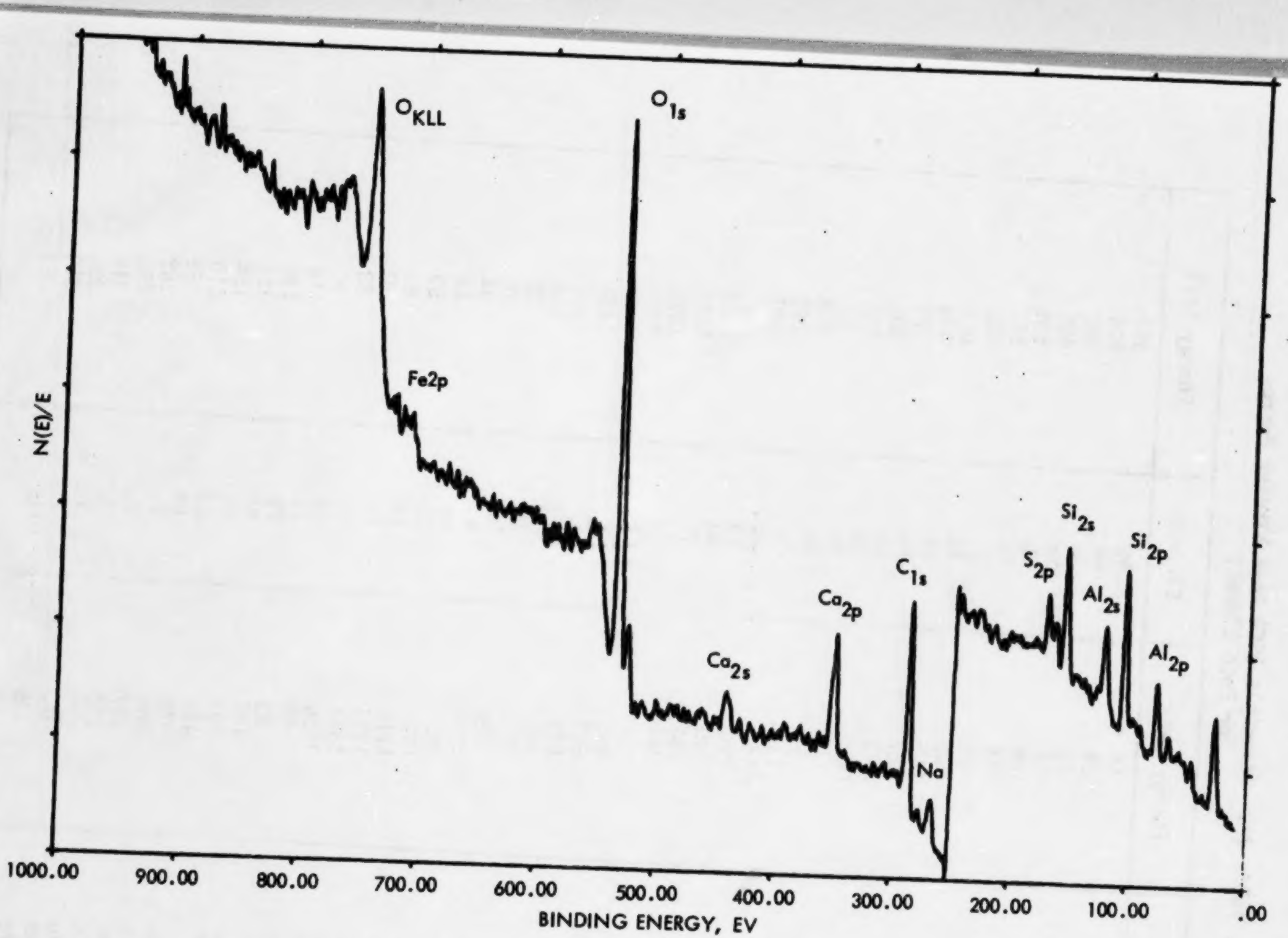


Figure 19. Survey ESCA Spectra of Particulate Matter from Fluidized Bed Combustor

Table 22. Principle ESCA Peak Binding Energy for Each Element

Element	Energy (eV)	Element	Energy (eV)
H	14	Ag	367
He	25	Cd	404
Li	55	In	443
Be	111	Sn	485
B	188	Sb	528
C	284	Te	572
N	399	I	620
O	532	Xe	672
F	686	Cs	726
Ne	867	Ba	781
Na	1072	La	832
Mg	1305	Ce	884
Al	118	Pr	931
Si	99	Nd	978
P	135	Pm	1027
S	164	Sm	1081
Cl	200	Eu	1131
A	245	Gd	1186
K	294	Tb	1242
Ca	347	Dy	1295
Sc	402	Ho	1351
Ti	455	Er	1409
V	513	Tm	1468
Cr	575	Yb	487
Mn	641	Lu	506
Fe	710	Hf	18
Co	779	Ta	25
Ni	855	W	34
Cu	931	Re	45
Zn	1021	Os	50
Ga	1116	Ir	60
Ge	1217	Pt	70
As	1323	Au	83
Se	1436	Hg	99
Br	69	Tl	118
Kr	89	Pb	138
Rb	111	Bi	158
Sr	133	Po	184
Y	158	Rt	210
Zr	180	Rn	238
Nb	205	Fr	268
Mo	227	Ra	299
Tc	253	Ac	319
Ru	279	Th	335
Rh	307	Pa	360
Pd	335	U	381

In practice a beam of inert (typically Ar) or reactive gas ions (O_2) generated in a duoplasmatron are accelerated to 15-25 keV. Using electrostatic lenses, a beam of 2-10 μm at $\leq 1 \times 10^{-9}$ A ion current is produced. These primary ions as they impact cause the upper atomic layers to be sputtered or stripped off. The material that leaves is mostly composed of neutral atoms or molecules, but a small fraction is ejected as positive or negative ions. These secondary ions are extracted into a double focusing mass spectrometer with a typical resolution on the order of 300 to 5000 for mass/charge separation. Ion detection is accomplished using electrical or photographic devices. For surface analysis work electrical detectors using discrete and continuous dynode multipliers and the Daly-type detectors(109) are most commonly employed. Signal processing and data manipulation are performed with the aid of dedicated mini-computers.

An IMMA beam can be used in a stationary mode for localized analysis or rastered over the surface for survey analysis. When the beam is rastered over the surface, the mass spectrum is taken in the analogue recording mode as the sample atoms are sputtered. The ion intensities are quantitatively determined by counting the mass or masses (elements) of interest for a preset time. In this mode elemental mapping can be performed by using the intensity of a specific ion to modulate the intensity axis of an oscilloscope, which is synchronized with the rastering beam. Figure 20 taken from McHugh (110) shows the Ti and B rich inclusions near a grain boundary in an inconel alloy sample obtained using this elemental mapping procedure.

As a natural result of the secondary ion production, successively deeper layers of the sample are exposed as the beam is rastered over a given area. Depth profile measurements are performed by monitoring the mass (or masses) of interest while rastering the primary beam on an area of at least 5 or 6 beam diameters on a side. In this manner a flat bottom crater is produced so that by proper gating of the detector counting electronics, only those ions generated from the flat bottoms are collected and counted.

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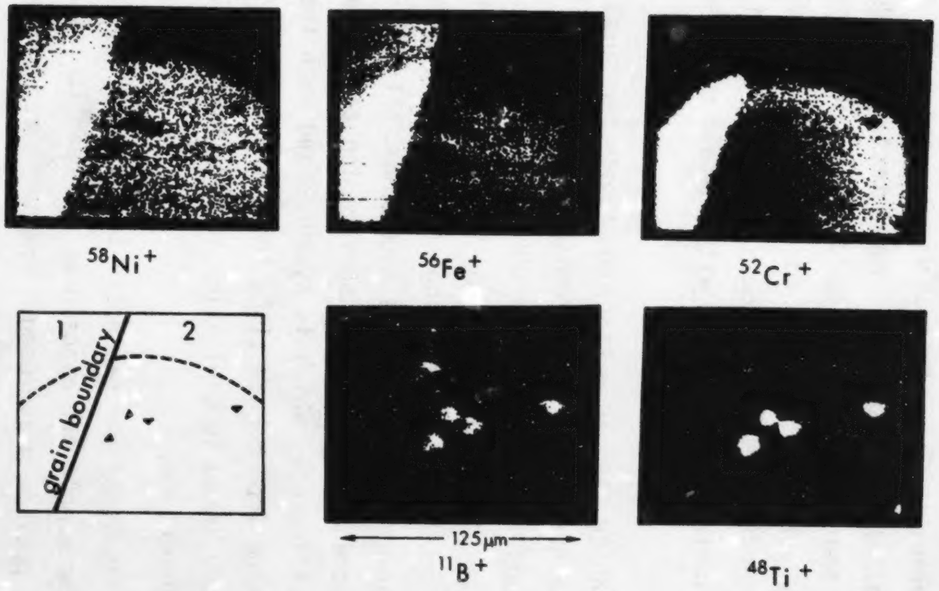


Figure 20. Elemental Inclusions in Inconel Alloy Using IMMA

The depth resolution will depend directly on the beam energy: the higher the kinetic energy of the primary ions, the more the ions penetrate and stir the upper atomic layers. Additional factors such as 1) mean escape depth of secondary ions, 2) recoil implantation, 3) molecular ion interferences, 4) primary beam induced diffusion of matrix species, 5) non-uniform sputter removal of matrix layers, and 6) implanted primary ion chemical and lattice damage effects will tend to reduce the depth resolution of IMMA. While it is theoretically possible to see a monolayer, practical considerations reduce the resolution to ∿25-50 Å. For a more detailed discussion of these problems, see References (111, 112, 113). Figure 21 is a sample depth profile by IMMA on a sample of fly ash taken from a coal fired power plant. Only Si, Ca, Fe, Cu and Au are plotted. Each element monitored was ratioed to Al to normalize the data and to enhance the response to surface layers. Since a surface layer would shield the fly ash, the main source of Al, the element to Al intensity ratio would be increased and produce clearly defined inflection points in the depth profile curve. The Au was vapor deposited as part of the sample preparation and shows what a surface layer would look like on SIMS elemental depth profiles. Fe, Cu, and Si were fairly constant at all depths, but Ca exhibited an increasing concentration with depth.

Sensitivity - ESCA

The observed intensity of an ESCA signal is a function of the element and its concentration on the surface of the material studied. The most important factor in being able to estimate the quantity of an element present is the efficiency with which the X-rays are absorbed by the atoms in the sample. If the cross section for X-ray absorption for an atomic subshell is low, the resulting ESCA sensitivity for those electrons (element) will be low. Scofield (114) has published a list of elemental sensitivities and Swingle (115) has normalized them to relative to C 1s. In practice the observed peak intensities are corrected to the relative intensity ratios in Scofield's table before the abundance or normalized percentage composition of the surface is calculated. Each element's peak height (PH_e) for a selected electron is measured, then multiplied by the intensity factor (IF) and a scale correction factor (SF) to obtain a

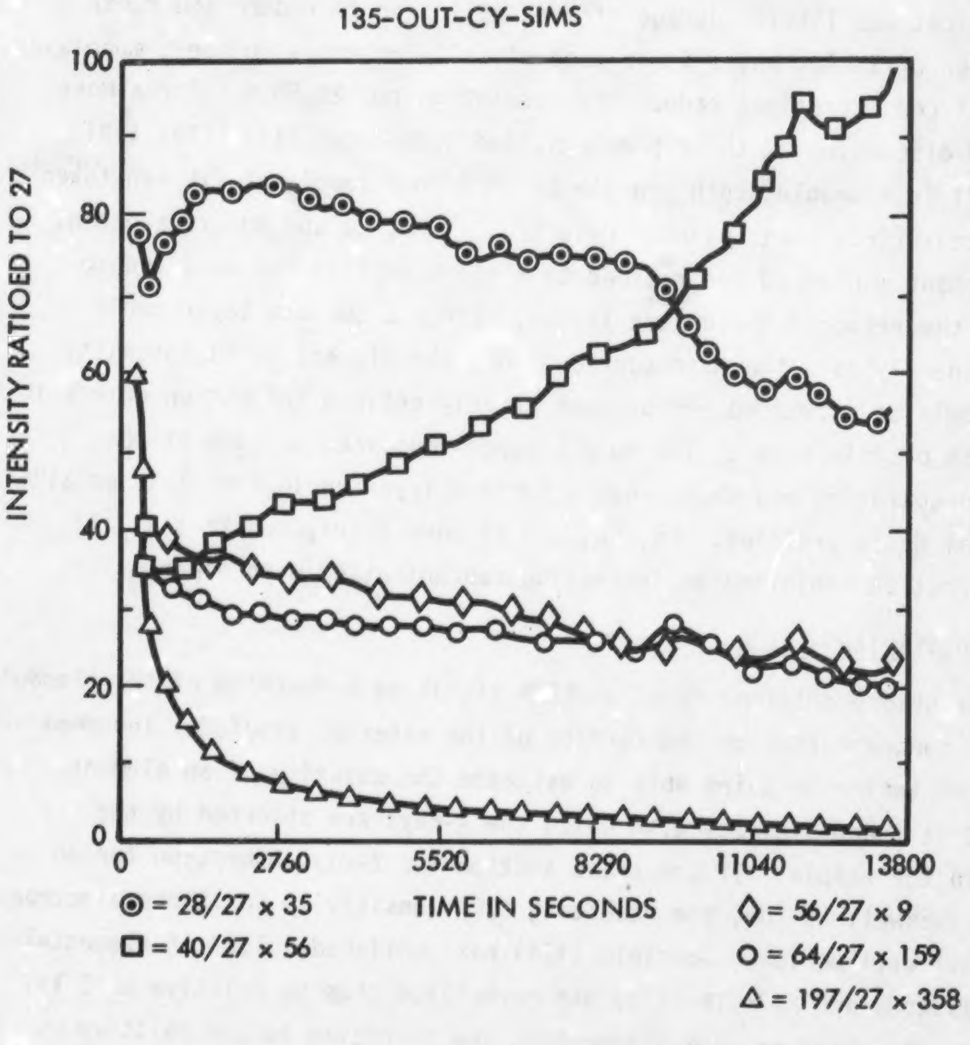


Figure 21. Depth Profile Analysis
of Fly Ash Sample Using IMMA

normalized peak height (PH_n). Thus: $PH_n = (PH_e)\ (IF)\ (SF)$. All the normalized peak heights are summed and the individual normalized percentage distribution can be determined:

$$\%\ \text{Distribution Element X} = \frac{PH_{n,x}}{\sum_{x=1}^{\infty} PH_{n,x}} \times 100\%$$

For the spectra in Figure 19 the normalized surface (15-40 Å) composition was: Fe-1%, O-53%, Ca-10%, Na-1%, S-5%, Si-16% and Al-15%. Most elements can be detected at 0.1% abundance with a 10-15 minute data acquisition time, but under favorable circumstances detection limits have gone as low as 0.001%.

Sensitivity - SIMS - The question of sensitivity is quite complex and is imminently bound with the processes which generate the secondary ions. In the simplest sense the generation of secondary ions can be thought to occur via two ionization processes: 1) kinetic ionization and 2) chemical ionization (110, 116, 117, 118).

The kinetic process occurs when inert ions are used to bombard a surface. The transfer of energy during the beam penetration causes lattice bonds to be broken and the ejection of some atomic electrons into the conduction band of the material. Most of the ions produced this way are neutralized before they leave the surface. However, these neutral atoms retain a great deal of energy and can lose an electron via Auger or quantum deexcitation processes to produce an ion for mass analysis.

Chemical ionization processes require that a chemically reactive species be present to reduce the number of conduction electrons available for the neutralization of ions. Oxygen typically is a good example, since it forms many compounds which would render the region surrounding the beam non-conductive. If oxygen is not present in the sample, then it can be used as the bombarding ion to increase the number of ions emitted.

In most materials the chemical ionization mechanism produces the majority of ions. For this reason oxygen bombardment is most commonly used to reduce the differences in ion production from a specific element caused by matrix changes.

The sensitivity of a SIMS instrument will also depend on good collection and detection efficiency. Assuming an average atomic weight of 100, an ionization efficiency of 20% (ions/element), a mass spectrometer efficiency of 10%, and 6 ions over a few seconds period required for detection, a detection limit of 10^{-19} grams can be expected(104). Ionization efficiencies of the order postulated can occur for positive ions of alkali metals and negative ions of halogens. For other elements ion yields of down to 10^{-5} can be expected, with the expected reduction in sensitivity. Correction factors for ionization efficiency, isotope abundance and matrix are normally included in some form in the software of the instrument.

Instrumentation - ESCA - Figure 22 (taken from a McPherson ESCA 36 manual) diagrams the key components of an ESCA system. Essentially an ESCA spectrometer consists of sample chamber with an X-ray source (usually Mg) which is kept below 10^{-5} torr. The electrons ejected from the sample are analyzed using an electrostatic energy analyzer and are detected by an electron multiplier. Scan and readout systems used in ESCA instrumentation are either of a continuous or incremental type. Most often the incremental scanning mode is employed so that signal averaging can be achieved by performing repetitive scans over the energy region of interest. Most commercial systems employ a dedicated minicomputer to store the data for later manipulation and display.

Instrumentation - SIMS - Figure 23 shows the key components in an ARL IMMA. SIMS units use a duoplasmatron for its ion source. This source uses both electrostatic and magnetic constriction to produce a high brightness source. The beam is focused using electrostatic lenses and can be rastered for imaging or depth profile work. Vacuums of 10^{-8} to 10^{-11} torr are commonly found in the sample chamber. The mass spectrometer for IMMA units is normally a double focusing (electrostatic and magnetic) device with a resolution of between 300 to 3000 depending on the

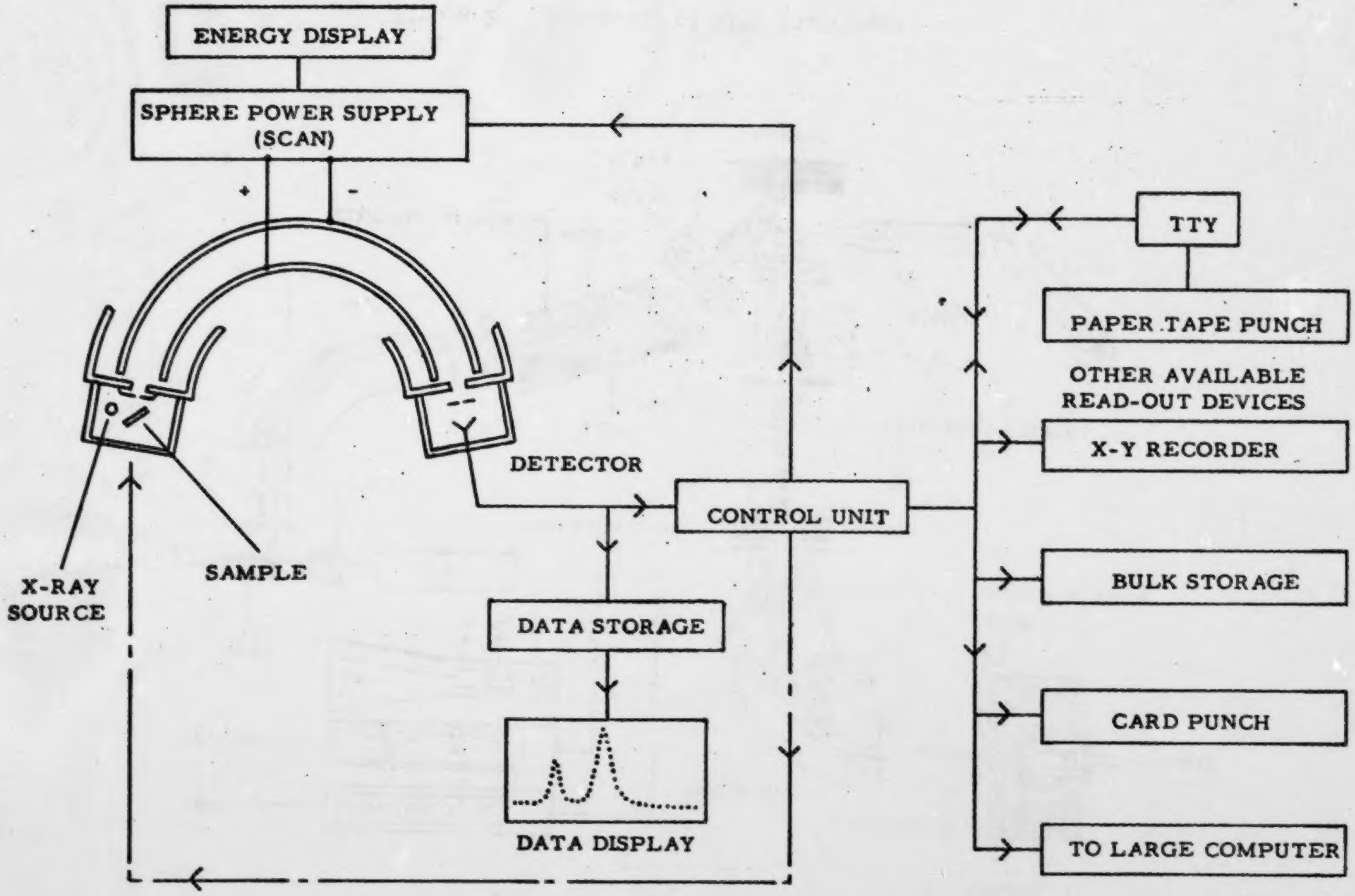


Figure 22. Block Diagram of McPherson ESCA 36

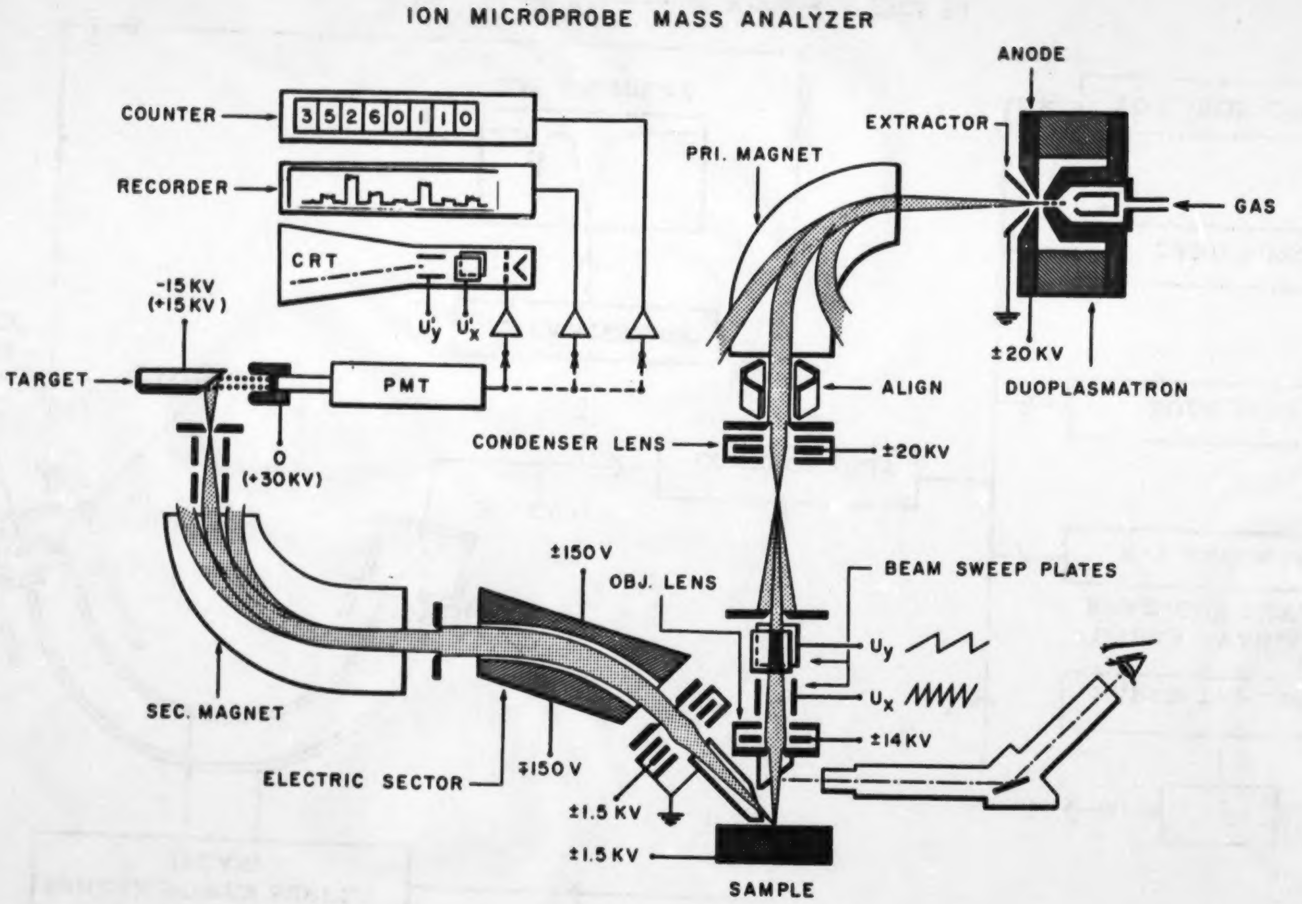


Figure 23. Schematic of SIMS Instrument

instrument. Electrical detectors employing either discrete or continuous dynode electron multipliers or Daly-type detectors are used. Signal processing and data manipulation is accomplished using a dedicated mini-computer.

3.3.2 Sampling Handling/Preparation for ESCA and SIMS

ESCA can analyze gases, liquids and solids, but since it is a vacuum technique low vapor pressure solids are most easily run. This discussion will only cover the mounting of loose particles or solids for ESCA analysis.

A variety of methods for mounting particles is available. The most common method used is to spread a thin layer of sample over the surface of a double-sided adhesive tape. Unless the surface is completely covered, the tape will provide a background signal and under the combination vacuum, X-ray, and etching beam, it may decompose or deposit an organic film on the particles. This is not important unless carbon is to be analyzed in the sample. The main problem is that the tape insulates the sample and surface charges can be built up as the ESCA electrons are ejected. The increased surface charge (positive) retards the ejection of the electrons, causing a shift in the spectrum, while the non-uniformity of surface charge causes line broadening.

There are two recommended approaches based on TRW's use of ESCA and SIMS. The first is a variant of the double-sided adhesive tape approach and it is called the "sticky gold" mounting approach. A piece of double-backed adhesive tape is placed on a sample stage, and then a light film of gold is vacuum deposited over the tape. A small drop of carbon or silver paste is applied to an edge of the now gold-coated tape to ensure electrical contact with the stage. Enough sample to completely cover a 4 x 4 mm area is then placed onto this conductive sticky surface and lightly pressed with a glass microscope slide to attach it securely. For added conduction an additional layer of gold or perhaps carbon can be placed on the now mounted sample as shown in Figure 24.

Another approach (115) is to put an excess of the sample in a folded indium strip and hand press it into the soft foil. The main advantage

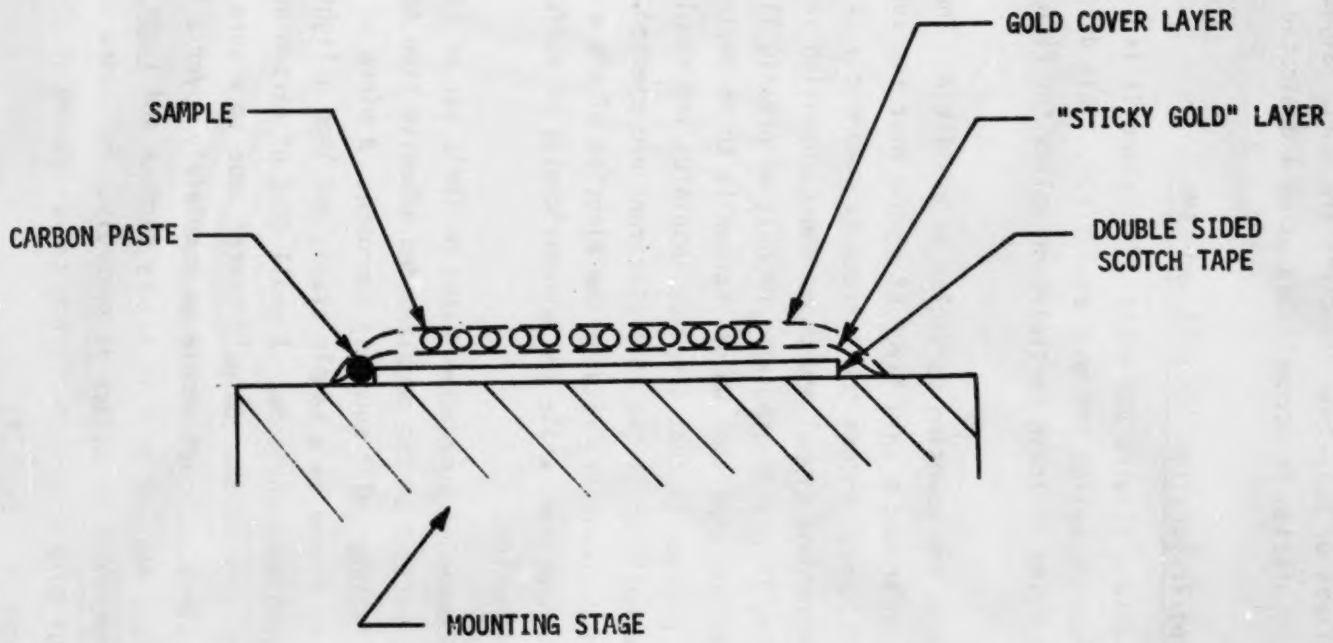


Figure 24. Sticky Gold Mounting Technique

is that a clean unworked surface is presented for analysis. Usually (as with the sticky gold) the surface is completely covered, so that only the sample is analyzed.

SIMS like ESCA can have surface charging problems which will affect the analysis of non-conductive materials. The same mounting procedures for ESCA can be used for SIMS. It is especially recommended that the "sticky gold" procedure be employed for SIMS. This procedure was actually developed for SIMS work by TRW and has been found to eliminate any mounting or charging problems.

3.3.3 Compound Identification

The primary role of ESCA and SIMS in this analysis scheme is to provide information on surface concentrations of trace elements. Inherent in ESCA and SIMS is the ability to perform compound identification operations. The following sections briefly discuss the compound identification abilities.

Compound Identification - ESCA

A unique trait of ESCA is the ability to determine the chemical environment of an atom. ESCA is able to do this because the binding energies of the core electrons are influenced by the valence electrons and thus the chemical environment of the atom. If one of these valence electrons is removed, the amount of shielding of the core electrons from the nucleus is diminished. The effective nuclear charge experienced by the core electrons increases, and thus the E_b is increased. In the simplest case a shift in an ESCA line reflects a change in the oxidation state of an element. In general any parameter (i.e., oxidation state, ligand electronegativity, coordination) that affects the electron density about the atom is expected to result in a chemical shift in electron binding energy. The shift is frequently on the order of 1 eV per unit change in oxidation state. Consequently high resolution ESCA can tell the difference between species like C or CO_3^{-2} and S^{-2}, SO_3^{-2}, and SO_4^{-2}. An example of sulfur chemical shifts is shown in Figure 25, which is a high resolution ESCA spectrum at 100 Å depth for >27 μm particles collected from an FBC unit. The surface high resolution spectrum showed only S^{+6},

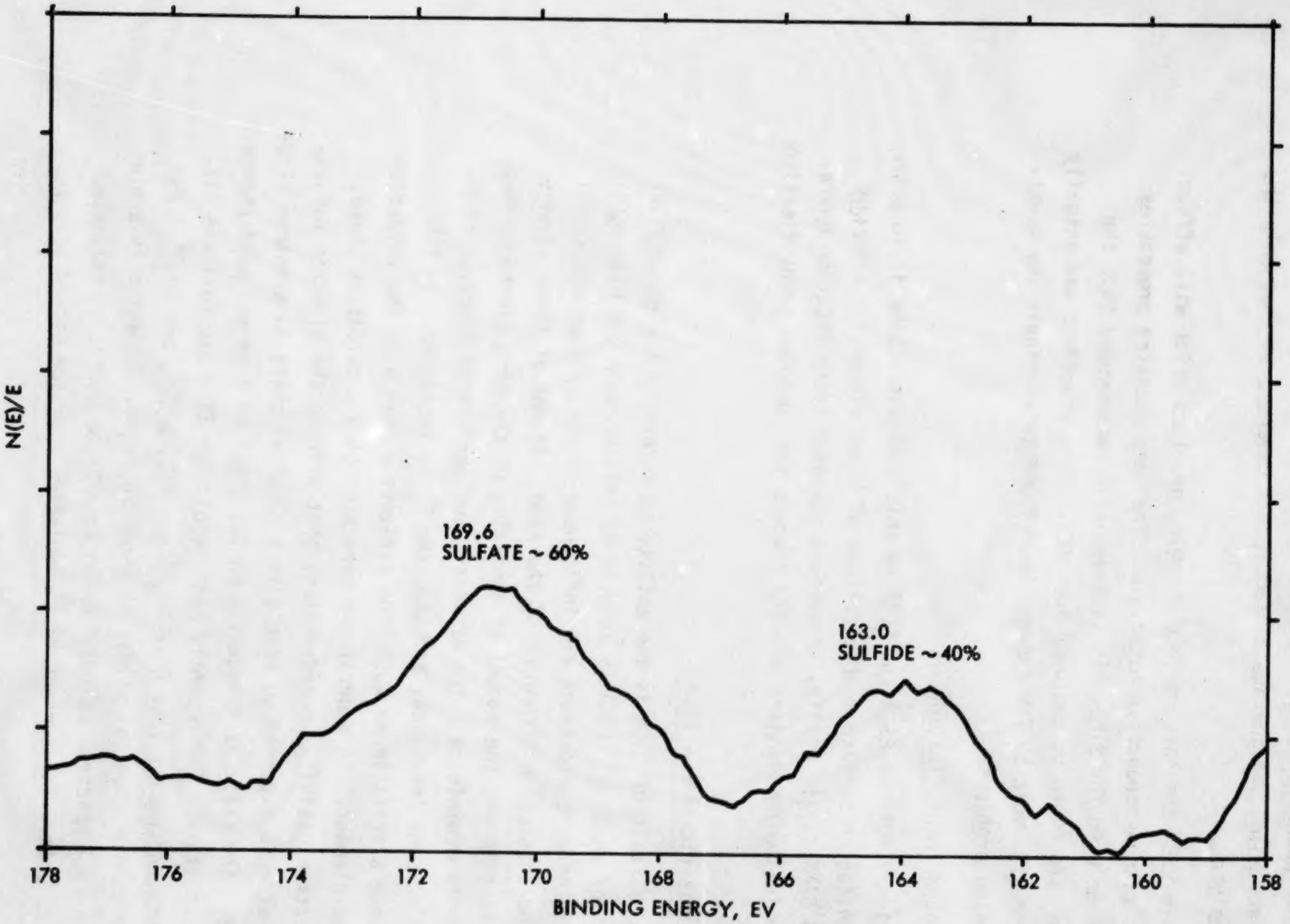


Figure 25. High Resolution ESCA Spectrum Showing Chemical Shift for S^{-2} and SO_4 Compounds

but after removing the top layer with an Ar^+ beam a layer or particle of S^{-2} was uncovered. The surface S^{+6} was probably due to air oxidation of this sulfide particle. The same result was found by Werner (119) at another FBC.

Compound Identification - SIMS - Unlike ESCA, chemical compound information is not directly obtainable from IMMA. An IMMA, however, can obtain elemental information from a localized region, to determine the exact elemental ratio at the surface, in an inclusion, or of a discrete particle. In many cases the software provided by the manufacturer will include correction factors applicable to many matrices. If these correction factors are not applicable to the environmental samples studied, then an empirical procedure must be employed.

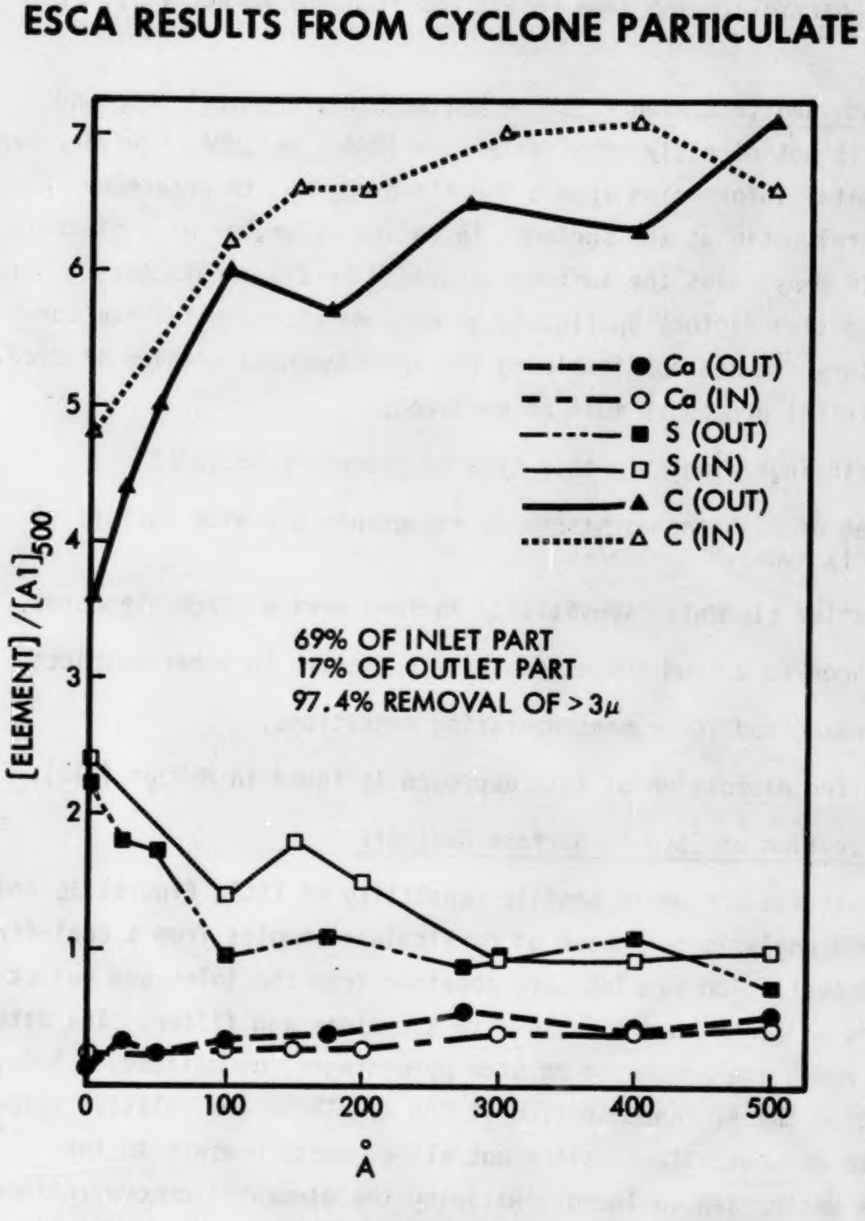
The basic ingredients in this type of procedure include:

- A set of homogeneous standards representing a wide variety of matrix types.
- Relative elemental sensitivity factors derived from standards.
- Methods to extend these sensitivity factors to other matrices.
- Standardized instrument operating conditions.

A detailed discussion of this approach is found in McHugh (110).

3.3.4 Application of ESCA to Surface Analysis

To illustrate the depth profile capability of ESCA, Figures 26 and 27 show the ESCA analysis performed on particulate samples from a coal-fired power plant test. The samples were obtained from the inlet and outlet of an FGD using an EPA Method 5 train with a cyclone and filter. The data for Ca, C, and S are presented as atom percentages, normalized to 100%, and ratioed to the Al concentration at 500 Å. These are relative values, not absolute concentrations, since not all elements present in the particulate matter are included. Ratioing the elemental concentrations to the Al concentration at 500 Å accentuates any surface concentration and tends to normalize any analysis errors.



ESCA RESULTS FROM CYCLONE PARTICULATE

Figure 26. ESCA Depth Profile Analysis of $\geq 3 \mu m$ Particulate Matter before and after an FGD.

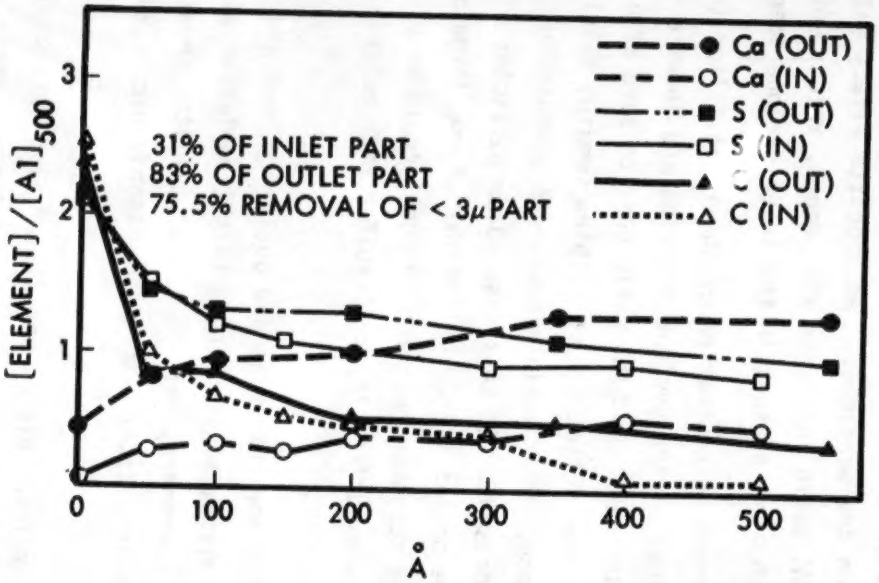


Figure 27. ESCA Depth Profile Analysis of <3μm Particulate Matter before and after an FGD.

Relative concentrations for the Method 5 cyclone (particulates >3 μm) show that the sulfur/aluminum ratios for both the inlet and outlet particles are high at the particle surface and decrease with depth. This type of data would be expected if a volatile compound of S were adsorbed or condensed on the particles. Note that the sulfur concentration tended to level out above zero, indicating that the coated particle contained sulfur. Subsequent XRD analysis confirmed the presence of $CaSO_4$ in the inlet and outlet cyclone catches. The sulfur rich surface layer was probably formed by H_2SO_4 condensing on the particles. An opposite effect was seen for the carbon, where the C/Al ratio increased with depth, which indicates that unburned coal particles are present in the inlet cyclone sample.

The relative carbon concentration of the inlet filter (<3 μm) particles is much lower than that of the cyclone fraction and shows a sharp surface dependence. Interestingly, the C/Al ratio goes to zero after 400 Å for the inlet samples but in the outlet filter samples remains fairly constant after the initial drop. Once again a substrate containing small amounts of carbon might be present. In this case <3 μm particles of unburned coal (concentrated in the outlet filter by removal of the large particles by the FGD) or $CaCO_3$ (a scrubber reaction product) could be present. The S/Al ratio indicates a surface layer of sulfur rich material similar to that found in the cyclone catch.

The Ca/Al ratios for the inlet and outlet cyclone and inlet filter samples are very similar, all showing a slight depletion at the surface and roughly equivalent concentrations. The outlet filter shows a higher concentration of Ca, which, after 100 Å, corresponds nicely with the S concentration.

Catches from impactor plates and filter also were analyzed by ESCA to determine relative concentrations at the particle surface as a function of particle size. An interesting relationship was found when the Ca/S ratio was determined by selected particle sizes and at various depths, Table 23. The first two stages exhibited mixed trends that might be due to a mixture of fly ash and a Ca-S compound coated with H_2SO_4. The particles in the 8.5 and 3.5 μm size fraction appear to be primarily a Ca-S compound with

Table 23. ESCA Data - S/Ca Ratio by Particle Size (μm) and Depth (Å)

Depth (Å)	Average Geometric Aerodynamic Diameter (μm)							
	53.9	20.2	8.5	3.5	1.8	0.9	0.51	0.29
Surface	2.78	3.23	-	1.35	5.56	7.69	-	-
100-500	4.55	2.50	0.83	1.28	1.52	7.14	6.25	11.11
500	-	-	1.16	1.00	0.93	4.76	5.00	2.94

(-) ESCA spectra not run

little or no coating of H_2SO_4. The particles in the 1.8 μm fraction exhibit a strong coating of H_2SO_4 on a Ca-S particle. Finally the last three stages show a thick coating of H_2SO_4 and may represent H_2SO_4 droplets formed when the H_2SO_4 vapor entering the FGD was rapidly cooled in a stream of fine particles.

Identification of these Ca-S compounds might have been made using the ESCA system in the high resolution mode to identify sulfur's oxidation state. While this approach was not taken, additional XRD identification work on the bulk samples identified $CaSO_4$ and $CaSO_3$.

3.4 Summary of Bulk Composition Characterization

The methods presented in this section are the primary tools used for direct inorganic compound identification. Of the three discussed in Section 3.0, XRD is the method most specific for compound identification; however, it has several weaknesses. XRD cannot identify non-crystalline compounds, and its sensitivity is normally limited to compounds present at or above 0.1%. In order to offset these fundamental weaknesses, FTIR and ESCA (SIMS) have been grouped with XRD in this phase of the analysis scheme. FTIR provides functional group (anion) identification, some compound identification (crystalline and non-crystalline), and specialized analysis techniques (subtraction/addition of spectra). ESCA provides specific information on the oxidation state of the elements, but its primary use is to provide elemental and compositional information about the surface of the material studied. Figure 28 diagrams the relationship and the application of these three techniques.

One must always compile and interpret the data of previous analyses and use it to direct later analyses. In the Initial Sample Characterization phase, the Level 1 data were used to develop a list of compounds for analysis. In the Bulk Composition Characterization phase, the accurate quantitative elemental and anion data determined in the initial sample characterization phase were used to estimate the concentration of potential compounds. These concentration estimates determine whether a compound can be seen by XRD or FTIR. For example, to confirm the presence of a suspected compound, the region around its primary diffraction lines could be step scanned for a longer period of time to improve sensitivity. Similarly, the number of FTIR scans taken can be increased to improve the signal to noise ratio and the sensitivity. This is not to imply that survey scans are not run. Survey scans of the sample are necessary to provide information not found by other methods, and to insure the completeness of the overall analysis. Whenever compounds are known or suspected, however, a focused analysis is used to confirm or deny its presence.

It is suggested that an FTIR scan be run prior to the XRD analysis so that the compound information derived is available to aid the interpretation of the XRD spectra. Figure 28 shows two pathways: a sample scanned as received with an emphasis on far IR spectral data to identify transition metal anions and a surface study using acid (or water) extraction to remove surface compounds. Subtraction of the latter spectra from the former will emphasize those bands (compounds) associated with the surface which can be compared with the ESCA results. Further uses of the subtraction capabilities of FTIR were noted in Section 3.1.

After the FTIR spectra are run and interpreted, the XRD work can begin. The goals of the XRD studies are threefold: (1) study the overall make-up of the sample, (2) identify compounds from the list refined by the Initial Sample Characterization, and (3) confirm the presence of any compounds deduced from FTIR or from the previous analyses. As mentioned

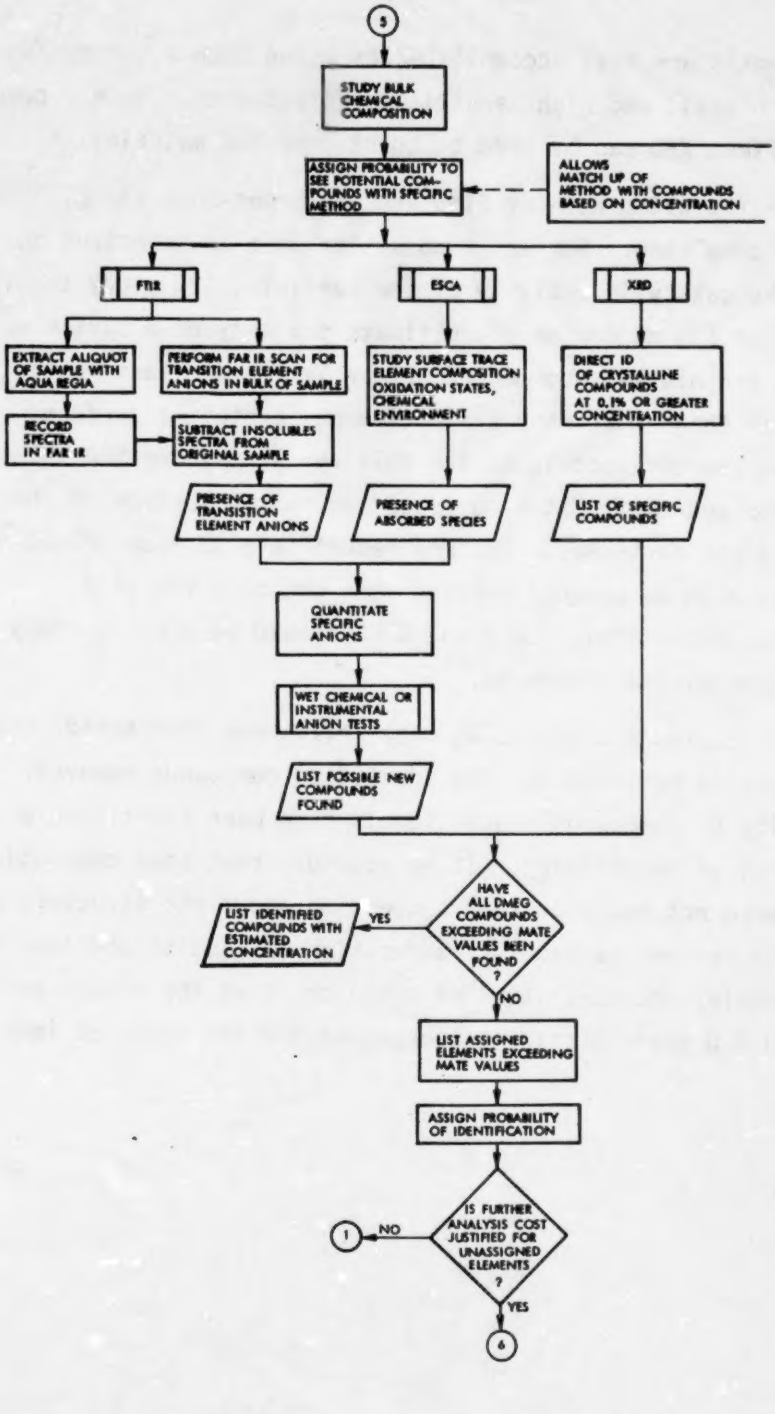

5
STUDY BULK CHEMICAL COMPOSITION
ASSIGN PROBABILITY TO SEE POTENTIAL COMPOUNDS WITH SPECIFIC METHOD
ALLOWS MATCH UP OF METHOD WITH COMPOUNDS BASED ON CONCENTRATION
FTIR
ESCA
XRD
EXTRACT ALIQUOT OF SAMPLE WITH AQUA REGIA
PERFORM FAR IR SCAN FOR TRANSITION ELEMENT ANIONS IN BULK OF SAMPLE
STUDY SURFACE TRACE ELEMENT COMPOSITION OXIDATION STATES, CHEMICAL ENVIRONMENT
DIRECT ID OF CRYSTALLINE COMPOUNDS AT 0.1% OR GREATER CONCENTRATION
RECORD SPECTRA IN FAR IR
SUBTRACT INSOLUBLES SPECTRA FROM ORIGINAL SAMPLE
PRESENCE OF TRANSITION ELEMENT ANIONS
PRESENCE OF ABSORBED SPECIES
LIST OF SPECIFIC COMPOUNDS
QUANTITATE SPECIFIC ANIONS
WET CHEMICAL OR INSTRUMENTAL ANION TESTS
LIST POSSIBLE NEW COMPOUNDS FOUND
HAVE ALL DMEG COMPOUNDS EXCEEDING MATE VALUES BEEN FOUND ?
YES
LIST IDENTIFIED COMPOUNDS WITH ESTIMATED CONCENTRATION
NO
LIST ASSIGNED ELEMENTS EXCEEDING MATE VALUES
ASSIGN PROBABILITY OF IDENTIFICATION
IS FURTHER ANALYSIS COST JUSTIFIED FOR UNASSIGNED ELEMENTS ?
NO
1
YES
6

Figure 28. Flowchart for Bulk Sample Characterization

earlier, these goals are best accomplished by using both a survey and spot scan to provide overall and high sensitivity information. Once a compound has been identified, XRD can be used to quantitate the material.

Surface studies using ESCA or SIMS are performed once the FTIR and XRD studies are completed. Surface composition data is important to: (1) determine the catalytic activity of the particle, (2) study the formation mechanism, or (3) determine the ultimate toxicity of a particle. Surface studies are highly recommended primarily for the last reason, since it has been shown that many trace elements exhibit a surface dependence. The reasons postulated for this result involve the volatility of some compounds and their later condensation on the surface of the already cool fly ash particles. The end result is a surface (25-50 Å) concentration as high as several percent when the bulk analysis indicate ppm concentrations. ESCA and SIMS should be used to study this and other surface-related phenomena.

Once the FTIR, XRD and ESCA/SIMS data have been interepted, the list of DMEG compounds is reviewed and the identified compounds removed. By this time the majority of compounds sought should have been identified or ruled out at some level of sensitivity. It is possible that some compounds of high interest were not found or that a question about the structure of the individual particles was raised. If a decision is made to continue the study of the sample, the next level of research is at the single particle level. Section 4.0 describes three techniques for the study of individual particles.

4. INDIVIDUAL PARTICLE ANALYSES

Once the analyst has completed both the initial sample characterization and the bulk sample characterization, information will be available ranging from gross physical characteristics through the identification of selected compounds. In the event that not all of the MATE compounds flagged from the SSMS results have been identified or ruled out, additional identification work can be performed using single particle analysis techniques. Analytical techniques (summarized in Table 24) which are suggested for identification of individual particles include:

- Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM-EDX)
- Electron Probe Microanalysis (EPMA)
- Transmission Electron Microscopy with Selected Area Electron Diffraction (TEM-SAED)

Extensive work (121 to 125) has been done in this area. The following sections will summarize the use of SEM-EDX, EPMA and TEM-SAED for single particle analysis.

4.1 Introduction to Electron Microscopy

When a collimated electron beam is focused on a sample, several phenomena, shown in Figure 29, can occur. As the beam impacts the sample, low energy (1-50 eV) secondary electrons are given off at the point of impact. Variations in the secondary electron emission intensity across the surface can be used to form an "image" of the surface, which is the technique of Scanning Electron Microscopy (SEM). The beam may cause ionization of an atom in the sample by knocking one of the inner shell electrons out of its orbital. In a manner similar to XRF, the inner-shell rearrangement may cause emission of an X-ray photon. Using an energy dispersive X-ray (EDX) or wavelength dispersive fluorescence spectrometer to detect these X-rays will permit the identification of the elemental composition of the area under the beam. If the sample is sufficiently thin, the electron beam will pass through the sample. Variations in the scattering cross-section of the sample cause the beam to penetrate at different intensities which is the basis for Transmission

Table 24. Summary of Methods Used for Individual Particle Characterization

Analysis Method	Principle of Operation	Information Derived	Compound Identification Procedure	Limitations
Scanning Electron Microscopy (SEM)/ Energy Dispersive X-Ray Spectrometer (EDX)	In SEM: - The specimen is swept by electron beam - Secondary electron emission intensity is recorded - The signal modulates brightness of oscilloscope beam, producing an image - Morphological characteristics of the specimen are determined from the image Using SEM in conjunction with EDX: - The secondary X-rays produced are monitored and individual elements present in the sample are identified and quantified	SEM system provides high resolution morphological information on individual particles The EDX attachment allows identification of individual elements in the particle Specific X-ray fluorescent wavelengths can be monitored to produce elemental distribution of the element (NOTE: These plots are especially useful for particles composed of various occluded materials) SEM information is a valuable adjunct to the PLM, especially for particles <0.5 µ (SEM magnifications are routinely in excess of 50,000X)	SEM's high resolution images often allow particle identification The EDX information can be used to determine elemental ratios and the exact composition of the particle	Relatively long counting times are required for trace elements, but the EDX instrument stability limits counting time to 10 or 15 minutes At high count rates, peaks may broaden Particles in close proximity may interfere and preclude unambiguous analysis EDX does not resolve elements from S to Ni very well Quantitative work depends on having suitable standards
Electron Probe Microanalysis (EPMA)	EPMA is used for elements above atomic Number 6 Small energetic electron beam impinges on surface of specimen, causing characteristic X-ray emissions which are analyzed by wavelength dispersion techniques For qualitative analysis: Wavelength positions are used For quantitative analysis: Peak heights (intensity ratios) are measures on both the unknown and on a standard of known composition	Obtains single particulate elemental composition of elements from carbon and above Many instruments use wavelength dispersive X-ray spectrometers and can resolve elements S through Ni	Compound identified by elemental ratios EPMA essential when elements C through Na are present since SEM-EDX does not see those elements	Identification possible only for particles containing discrete compounds rather than a homogeneous mixture Better quantitative results when standards are used whose composition closely matches the specimen
Transmission Electron Microscopy (TEM) - Selected Area Electron Diffraction (SAED) Analysis	In TEM, electron beam is impinged on a thin film of sample and the resultant transmitted electron beam is observed and recorded Quantitative analysis using TEM is superior to SEM because: ● Smaller samples can be observed and identified ● Chemical species such as asbestos are more reliably identified, (TEM's selected area electron diffraction analysis is more dependable than SEM's elemental analysis)	Provides high resolution photographs Produces single particle X-ray diffraction pattern	Identifies crystalline compounds by their characteristic diffraction patterns	Only crystalline material can be identified
Magnetic Density Gradient Selective Dissolution Separations	Magnetic separation is used to remove any magnetic material from rest of sample In density gradient separations, particles are floated in solvents of known density. Particles are separate by differences in their density Sample is extracted using selective dissolution (with different solvents)	Determines particles specific density magnetic characteristics, and solubility in solvents Main use is to reduce complex systems	Separating complex mixture into simpler fractions aids compound identification Can use information on particle density, solubility, and magnetic properties to identify compounds	Density gradient will only separate discrete particles; occluded material will have an average density Many compounds have solubilities in organic solvents used in density column Selective dissolution scrambles the compounds unless specific compound solvent systems can be found

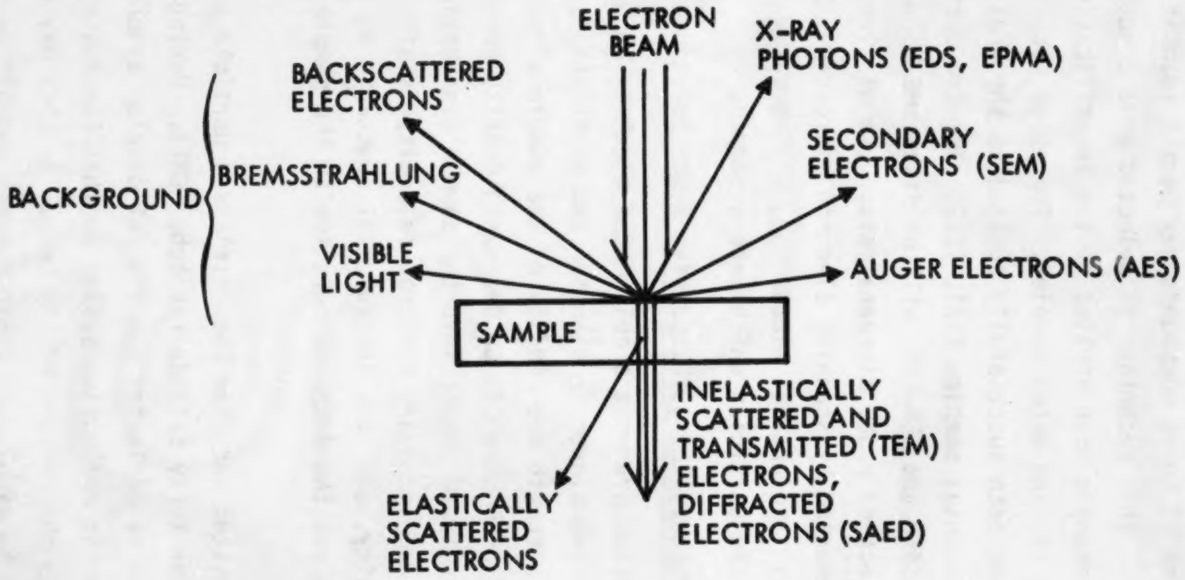

ELECTRON BEAM
X-RAY PHOTONS (EDS, EPMA)
BACKSCATTERED ELECTRONS
SECONDARY ELECTRONS (SEM)
BACKGROUND
BREMSSTRAHLUNG
VISIBLE LIGHT
AUGER ELECTRONS (AES)
SAMPLE
INELASTICALLY SCATTERED AND TRANSMITTED (TEM) ELECTRONS, DIFFRACTED ELECTRONS (SAED)
ELASTICALLY SCATTERED ELECTRONS

Figure 29. Interactions of an Electron Beam with a Sample

Electron Microscopy (TEM). Some of the incident electrons are backscattered causing a background signal. If the material is crystalline, a diffraction pattern may be formed similar to X-ray power diffraction except that the incident electrons are diffracted. Comparison of this pattern with patterns of known compounds may permit identification of the crystalline material. This technique of selected area electron diffraction (SAED) has for example been applied to the identification of asbestos (120) particles in air and water samples. The above techniques, in various combinations, have been successfully applied to the analysis of a wide variety of environmental samples (121, 122). The two most common of these combinations, TEM-SAED and SEM-EDX, will be discussed below, as well as the technique of electron probe microanalysis. Use of electron microprobe analysis, complemented by scanning electron microscopy, transmission electron microscopy, and optical microscopy, will greatly increase the analyst's knowledge of the particles which make a sample.

4.2 Scanning Electron Microscopy-Energy Dispersive X-Ray Spectrometry

An electron optical system produces a collimated electron beam focused on an area of up to one micron in diameter and penetrates to a depth of 2-5 nm. The beam strength and density of the sample affect resolution, since increased beam strength or decreased density permits the primary electron beam to penetrate deeper into the sample (increasing the volume range). Similarly, the secondary electron intensity is affected by sample composition and density, and such instrumental constants as the angles of the incident beam and the detector relative to the sample (instrument geometry).

Secondary electrons emitted when the beam strikes a particle are monitored and displayed on an X-ray cathode ray tube (CRT). During a scan of the sample, the beam is deflected and the CRT display synchronously moved by a coordinated magnetic deflection system so that the rasters of the CRT screen correspond to the rasters of the beam. In this way a visual image is produced which can be displayed, photographed, and stored on magnetic tape. The output of an SEM is a visual image of the surface topography of the sample. Resolutions of over 10 nm are available with typical magnifications available from 7X-240,000X. In addition to the enhanced magnification of SEM systems relative to optical microscopy, the depth of field of an SEM is 500 times that of an optical microscope.

The information available from such an image is similar to that of an optical microscope-shape, roughness, size and size distribution of particles, and homogenity of the crystal or particle. McCrone (19), besides the optical micrographs, has a complete SEM-EDX library, so that morphology can be used to identify particles below the range ($<1\mu$) of optical microscopes. In addition to using the morphological properties to identify compounds, the EDX attachment can provide individual particle elemental composition.

Chemical identification can be made by monitoring the X-rays produced by the electron beam with an energy dispersive X-ray detection system (EDX). The solid state lithium-drifted silicon detector normally used is placed as close to the indident beam as permitted to increase the intensity and the amount of signal fed through a multi-channel pulse-height analyzer coupled to a dedicated minicomputer. The detector is nonfocusing, so that secondary X-rays from outside the illuminated area caused by backscattered incident electrons will interfere. These secondary X-rays may be filtered with a carbon or beryllium window or the detector may be collimated to reduce the problem.

A spectrum may be taken for identification of the elements present, or the sample can be scanned for a single element. Typical sample time (excluding preparation) is 1 minute for major constituents, ten minutes for traces. Detection of components of a sample 1% or greater by weight are practical for the elements from sodium to uranium; however, quantitative analysis requires standards of a composition similar to the sample. In heterogeneous unknowns, it is not possible to construct such standards. Correction for the absorption of X-rays from each element by the other elements present and for the possible secondary X-ray emission caused by the excitation of one element by the X-ray of another must be made. For thin, flat surfaces, these corrections can be made through computer programs with an accuracy of typically 2-5% (123). Irregular surfaces, where the absorption path length is unknown, may have large errors. Subtraction of the Bremsstrahlung background and integration of the peaks are also performed by computer. The removal of the Bremsstrahlung background is complicated by its non-linear energy distribution and the presence of discontinuities in the background. By using the techniques of frequency filtering, the background can be successfully removed without significant increase in data reduction time. Removal of spectral interferences can be performed during computer reduction of the data from knowledge of the intensity ratios of major and minor peaks of each element identified. This is facilitated by the Gaussian shape of the peaks and the fact that typical interferences result from Kβ overlap with a Kα, so that the interference will be minor except when the elements are present in widely different concentrations.

Sample Preparation, SEM-EDX

Particulate matter for SEM-EDX analysis can be mounted on a number of types of material. Typically beryllium and carbon stages are used, since they produce no X-ray background. Other common mounting stage materials are aluminum and gold. Regardless of the stage material, a layer of Au, C or Pt is vapor deposited to ensure that electrical charge is not built up during the analysis. Charge build-up will cause the image contrast to be too white and might cause the particles to be repelled from the surface of the mounting stage. The latter possibility occurs when highly non-conductive particles are analyzed, and can be prevented by using the "sticky gold" mounting technique.

4.3 Electron Probe Microanalysis (EPMA)

Electron microprobe analysis, is very similar to SEM-EDX. Whereas the primary objective of SEM is the determination of surface morphology and has been modified to permit EDX, the objective of EPMA is the chemical analysis of a sample using EDX. As a consequence, several parameters vary significantly, although the hardware (electron gun, magnetic focusing, Si(Li) detector, multi channel analyzer/computer) is the same.

The sensitivity of EPMA is much higher due to the optimization of beam intensity over the illumination area. The beam diameters in EPMA vary from 0.1 μm to several microns whereas the SEM beam diameters are usually smaller than 0.2 μm. The increase in beam diameter permits beam currents of 10^{-6}-10^{-8} A for EPMA versus 10^{-11}-10^{-12} A used in typical SEM-EDX systems. As a result, detection limits in the ppm range are possible in EPMA. Electron microprobes are equipped with electron optical systems to permit location of the electron beam. Much lower magnification (approximately 3000X maximum) is attained than with the SEM due to image broadening at the higher beam currents employed in EPMA, and therefore much lower resolution is possible.

Quantitative electron microprobe analysis is best performed on flat, polished surfaces mounted in fixed geometries where emission of secondary X-rays (due to backscattered incident electrons), reabsorption of X-rays by the sample and secondary X-ray emission from primary X-ray excitation are minimized. Using a lithium-drifted silicon solid state detector, multichannel analyzer and dedicated minicomputer, major constituents (greater than 0.1% of the sample) may be analyzed individually or simultaneously in a typical time of 100 seconds with times of 1000 seconds typical for trace constituent analysis. The elements from oxygen to uranium can be determined. With concentrations greater than 10% of the sample, relative errors of ±5% can be expected (124) for most elements and higher relative errors, usually positive, for components less than 10% by weight. Detection limits depend on a number of parameters, including the orientation of beam; sample and detector and other geometric factors; data reduction procedure employed; and the morphology and composition of the sample itself. Typically, at longer count rates (1000 seconds) samples may be analyzed for components of several parts per million or more in a bulk sample. The method has been applied to analysis of ores and minerals (125), fly ash, atmospheric particulate aerosols, particles deposited in lung tissue and a large variety of other environmental samples. Sample preparation is similar to that for SEM-EDX.

4.4 Transmission Electron Microscopy-Selected Area Electron Diffraction

Transmission electron microscopy provides greater imaging capability than SEM and better detection of small particles due to the ability to control brightness and contrast. TEM also provides a field of view 2-3 times that of SEM. It also has the requirement, however, that samples must be thin enough to permit transmission of the electron beam. For such samples, TEM has the advantage that the internal as well as surface features can be observed since variations in the TEM image result from deficiencies in the scattering ability of the material sectioned. Biological or organic samples, thin metallic or nonmetallic films, for example, may be investigated. For samples opaque to the electron beam, a carbon film image of the surface may be made and the film subjected to TEM for observation of surface features of the object. In this manner the surface of samples too large or thick to be analyzed by SEM or normal TEM may be observed. Liquid solutions or suspensions may be evaporated onto a TEM grid for analysis.

As the electron beam passes through a crystalline sample, the electrons may be diffracted by the lattice. The diffraction pattern of a single crystal may be sufficient to identify the compound by comparison with the patterns of known compounds. The size of the crystal is critical, however. Typically, crystals below approximately 0.3 μm diameter give scattering intensities too low to permit accurate identification. At sizes of approximately 0.8 μm or greater, the crystal is opaque to the electron beam.

4.5 Summary of Individual Particle Characterization

Individual particle characterization is conducted to determine the specific morphological and chemical composition of the individual particles in a sample. It is also possible to use these techniques for compound identification of surface features on the particles themselves. SEM-EDX, EPMA and TEM-SAED should be applied sequentially (Figure 30) to allow the assessment of the results in light of the added cost and the benefits derived. The general approach for individual particle characterization using SEM-EDX and EPMA is to use accurate trace elemental mapping of a single particle to determine the empirical formula. SEM-EDX can also add high resolution morphology information on small particles (<0.5 μm) or on surface features. EPMA produces similar results for slightly larger particles (>0.2 μm), but has the added advantage of increased sensitivity and wider elemental range (> atomic number 6).

If a particle appears crystalline and cannot be identified by elemental mapping, then TEM-SAED can be employed. TEM-SAED should only be applied to the small particles or thin fibers. If surface features on a large particle are oriented properly (in relief), TEM-SAED is an excellent method to identify them.

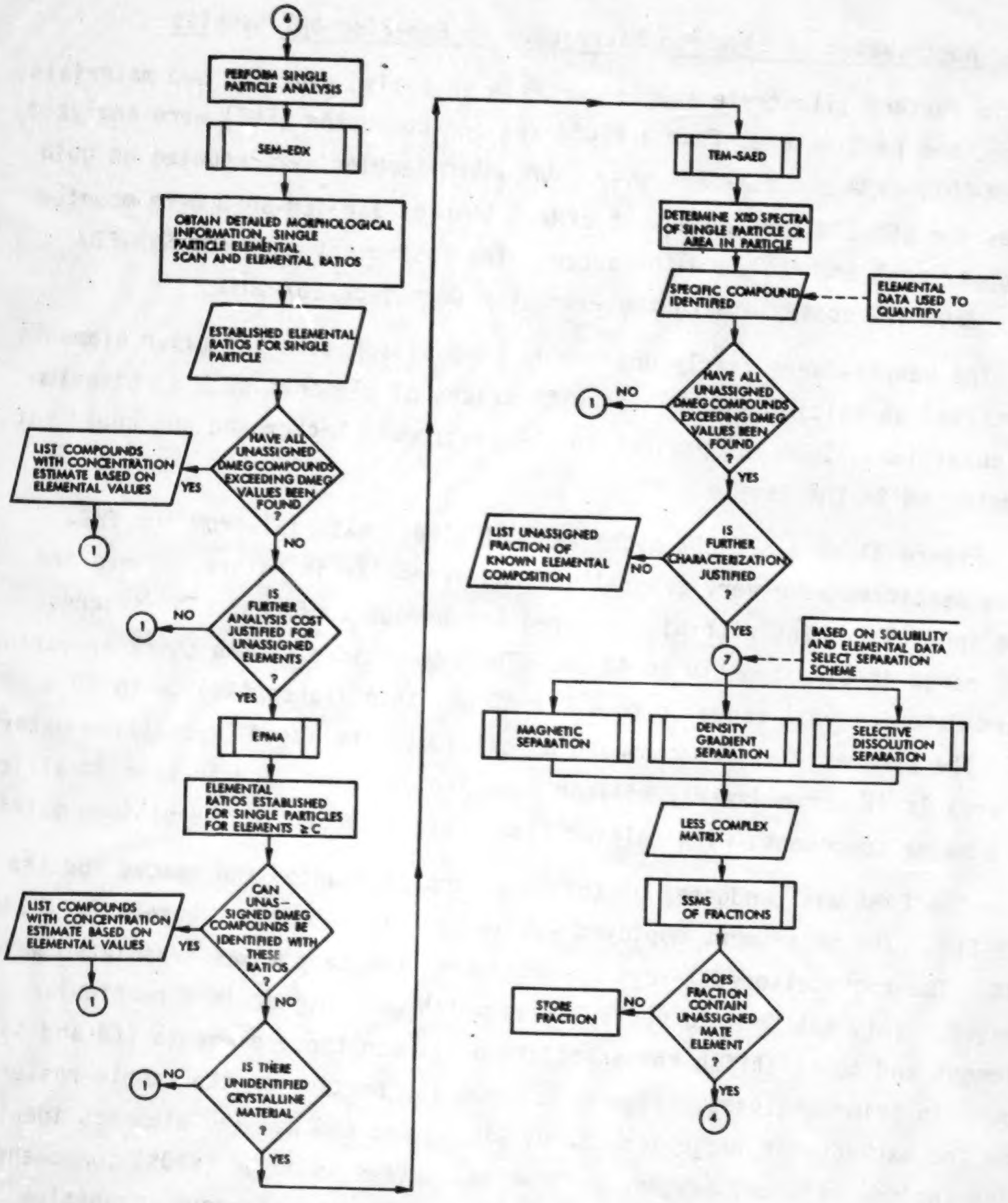

4
PERFORM SINGLE PARTICLE ANALYSIS
SEM-EDX
OBTAIN DETAILED MORPHOLOGICAL INFORMATION, SINGLE PARTICLE ELEMENTAL SCAN AND ELEMENTAL RATIOS
ESTABLISHED ELEMENTAL RATIOS FOR SINGLE PARTICLE
HAVE ALL UNASSIGNED DMEG COMPOUNDS EXCEEDING DMEG VALUES BEEN FOUND ?
YES
LIST COMPOUNDS WITH CONCENTRATION ESTIMATE BASED ON ELEMENTAL VALUES
1
NO
IS FURTHER ANALYSIS COST JUSTIFIED FOR UNASSIGNED ELEMENTS ?
NO
1
YES
EPMA
ELEMENTAL RATIOS ESTABLISHED FOR SINGLE PARTICLES FOR ELEMENTS ≥ C
CAN UNAS-SIGNED DMEG COMPOUNDS BE IDENTIFIED WITH THESE RATIOS ?
YES
LIST COMPOUNDS WITH CONCENTRATION ESTIMATE BASED ON ELEMENTAL VALUES
1
NO
IS THERE UNIDENTIFIED CRYSTALLINE MATERIAL ?
NO
1
YES
TEM-SAED
DETERMINE XRD SPECTRA OF SINGLE PARTICLE OR AREA IN PARTICLE
SPECIFIC COMPOUND IDENTIFIED
ELEMENTAL DATA USED TO QUANTIFY
HAVE ALL UNASSIGNED DMEG COMPOUNDS EXCEEDING DMEG VALUES BEEN FOUND ?
NO
1
YES
IS FURTHER CHARACTERIZATION JUSTIFIED ?
NO
LIST UNASSIGNED FRACTION OF KNOWN ELEMENTAL COMPOSITION
YES
7
BASED ON SOLUBILITY AND ELEMENTAL DATA SELECT SEPARATION SCHEME
MAGNETIC SEPARATION
DENSITY GRADIENT SEPARATION
SELECTIVE DISSOLUTION SEPARATION
LESS COMPLEX MATRIX
SSMS OF FRACTIONS
DOES FRACTION CONTAIN UNASSIGNED MATE ELEMENT ?
NO
STORE FRACTION
YES
4

Figure 30. Recommended Sequential Application of Individual Particle Techniques.

4.5.1 Application of Electron Microscopy to Experimental Samples

To further illustrate single particle analysis, overflow bed materials, sludge, and particulates from a fluidized bed combustor (FBC) were analyzed by SEM-EDX, EPMA and TEM-SAED (44). Uncoated samples were mounted on gold plates for SEM-EDX and subsequent EPMA. Samples for TEM-SAED were mounted on copper mesh and coated with carbon. The instrument used for SEM-EDX was a JEOL SEM equipped with the Princeton GammaTech EDX unit.

The samples were fairly uniform in composition with the major elements identified as calcium and silicon with traces of elements such as titanium and potassium. Iron was present in the instrument background and could not be detected in the sample.

Figure 31 is a SEM-EDX micrograph of sludge material from the FBC. These particles were very crystalline and irregular in nature. There are some spheres present with highly irregular porous surfaces. The spheres (2a) range in size from 10 to 40 μm. The dimensions of the thick appearing fused material (3b) range up to 100 x 60 μm, thin flakes (1c) up to 40 x 90 μm. The spheres (2a) are composed of calcium. The fused crystalline material in area 1c is predominately silicon with iron present, and in area 3c silicon is a major component, with calcium also present (fused in the silicon matrix).

The EPMA was conducted on the same samples mounted and imaged for the SEM-EDX. The instrument employed was an Applied Research Laboratories Model EMX. The backscattered X-rays produced when the sample was irradiated were imaged. This was done to verify areas which were higher in a particular element and to establish the association between those elements (Ca and S) found in prior analyses. Figure 32 shows the portion of the sample rastered and the backscatter image for Ca, O, Si, S, Fe, and K. The elements identified include calcium, oxygen, silicon and sulfur as major (>10%) components iron and potassium as medium (5-10%) components, and aluminum, magnesium chlorine, and titanium as low (1-5%) or trace (<1%) components. The EPMA already showed that Ca and Si exist in discrete areas, and that S showed no definite particle preference. Although in this application an area was rastered rather than a single particle, the technique of elemental mapping can be applied to single particles just as well.

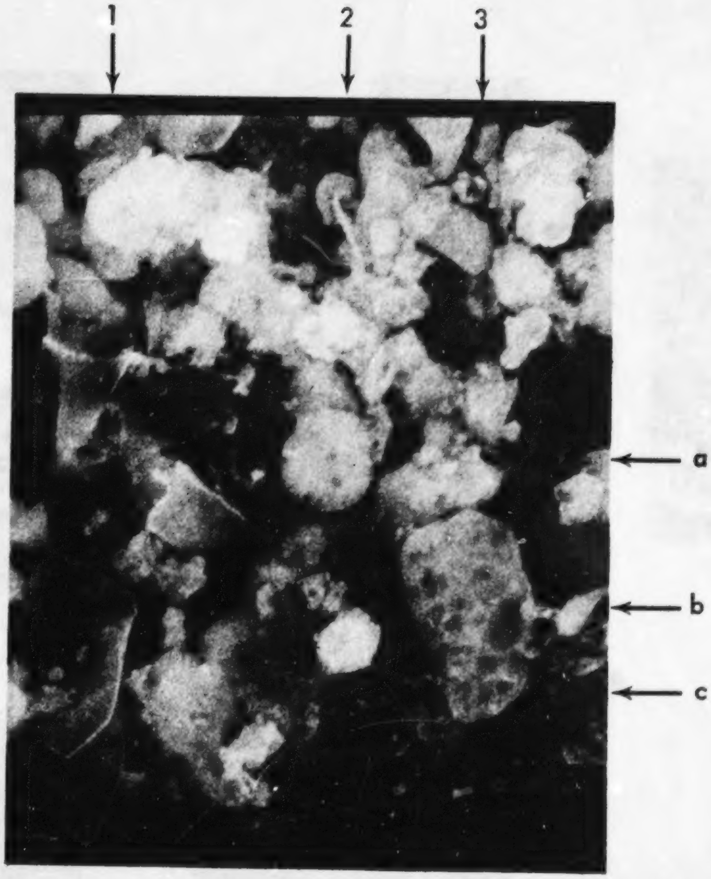
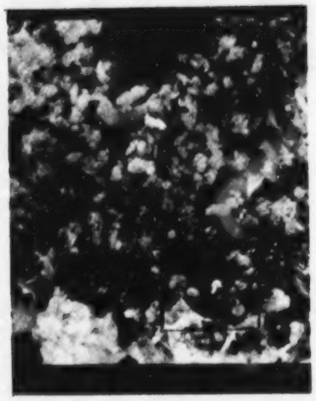
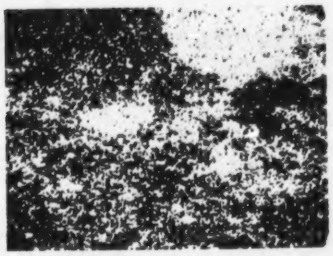


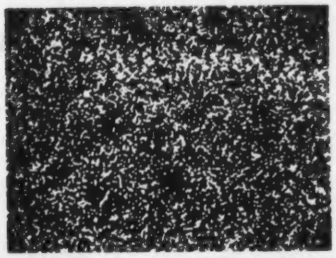
Figure 31. SEM-EDX at 3000X of Sample S-2-5



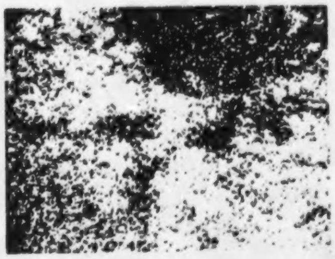
FLYASH
S-2-5



Calcium, Kα, Backscattered Image

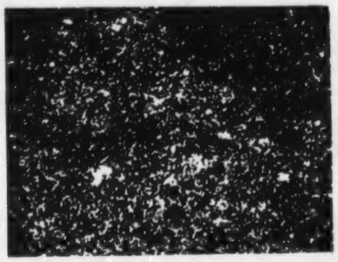


Oxygen, Kα, Backscattered Image

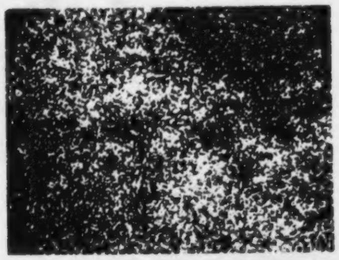


Silicon, Kα, Backscattered Image

Sulfur, Kα, Backscattered Image



Iron, Kα, Backscattered Image

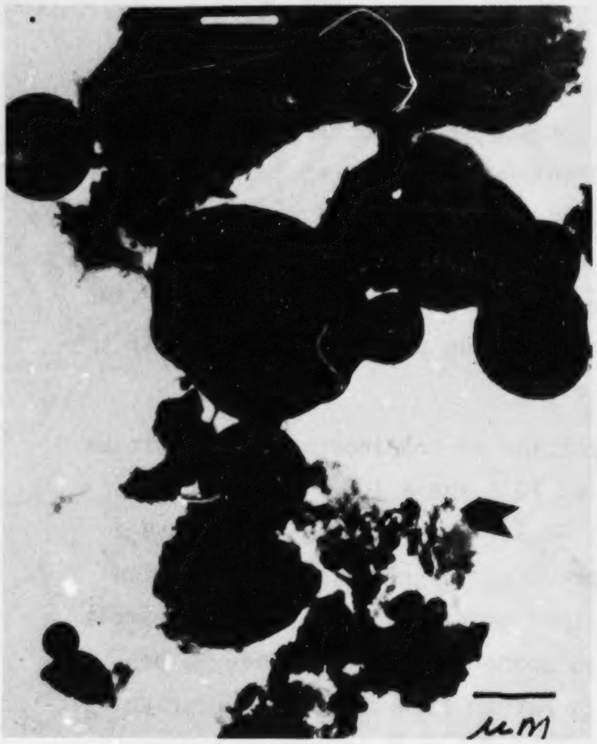


Potassium, Kα, Backscattered Image

Figure 32. EPMA Elemental Imaging of Sample S-2-5

Transmission electron microscope analysis with selective area electron diffraction was employed to assess the uniqueness of the individual particles observed in the SEM-EDX. Combining the information derived from SEM-EDX and EPMA can aid the analyst in describing the total number of the various species present. Many substances which appear essentially identical in elemental composition as measured with the electron probe will be determined by TEM-SAED to have unique diffraction pattern, allowing the identification of the material present.

The TEM-SAED system used in this portion of the inorganic work was an RCA Model EMU-3H. It had a resolution of 10 Å and a 100 kV beam. The accuracy of the determined d-spacing is ±0.5. Samples were mounted on a copper mesh coated with carbon. This provides for electron transmission and conductance. The TEM images are not of good quality due to the sample thickness, > 1500 Å. In most cases thin areas of the sample had to be chosen for electron diffraction analysis rather than uniquely appearing crystalline material. Nevertheless sample S-2-5 (Figure 33) is a good example of TEM/SAED application. In this case a definite fine crystalline material was imaged, isolated, and identified as SiO_2. These fine particulates were less than one micron in size.



TEM Image, Sample S-2-5.
Thin area analyzed using
SAED.

Electron Diffraction Pattern

Area Analyzed		
Determined d-spacings	Compound Identified	Literature d-spacings
4.41	SiO_2	4.26
3.14		3.34
2.64		2.46
2.28		2.28
1.93		1.82
1.48		1.54

Figure 33. TEM-SAED of Fibrous Material in S-2-5

5.0 SUMMARY

The Level 2 analysis procedures listed in this manual were selected and integrated into a scheme of analysis in order to be able to characterize completely most inorganic environmental samples. This analysis scheme will determine:

- Morphology of particles
- Thermal stability data
- Quantitative elemental data
- Quantitative anion data
- Direct identification of specific compounds
- Identification of compounds present on the surface of a particle
- Elemental depth profile data
- Valence state information on selected elements
- Elemental composition of individual particles
- Identification of surface features.

Even with these successes, the analytical paths presented in this document must be considered evolving ones. The main difficulty with inorganic Level 2 analysis lies in the direct measurement of species present at concentrations less than ∿1% but greater than trace (∿1 ppm). This measurement gap is not filled by any one compound isolation and quantitation technique. Future work by IERL should be applied in that measurement area and toward improving the specific procedures used in each method application.

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APPENDIX A

SPECIFIC ANION ANALYSIS PROCEDURES

APPENDIX A — SPECIFIC ANION ANALYSIS PROCEDURES

Summaries of specific anion tests for Br^-, I^-, $CO_3^=$, HCO_3^-, Cl^-, CN^-, F^-, NO_3^-, NO_2^-, $HPO_4^=$, $S^=$, $SO_3^=$, $SO_4^=$ are contained in the following sections. In addition to these anions, a specific test for NH_4^+ is also included. Brief summaries of the procedures, inferences, sampling, and limits of detection are given. Those methods taken from the EPA Water and Waste Water Manual have their Storet number listed, while ASTM procedures are referenced by their number.

A-1 AMMONIA (STORET NO. 00610)

Summary of Method

The sample is buffered at a pH of 9.5 and distilled into a solution of boric acid. The ammonia in the distillate is determined colorimetrically by Nesslerization (HgI_2, KI, NaOH).

Interferences

Glycine, urea, glutamic acid, cyanates and acetamide hydrolyze very slowly in solution on standing. At a pH of 9.5, urea hydrolysis amounts to about 7.0% and cycanates amount to about 5.0%.

Glycine, hydrazine, and some amines will react with Nessler's reagent to given the characteristic yellow color in the time required for the test.

Organic compound such as ketones, aldehydes, alcohols, and some amines may cause an off color on Nesslerization. Some organic compounds like formaldehyde may be eliminated by boiling at a low pH prior to Nesslerization.

Residual chlorine must be removed prior to the ammonia determination by pretreatment of the sample.

Sampling

Collect samples in accordance with American Society for Testing and Materials methods D510, D860, D1066, D1192, and D1496. If sample cannot be immediately analyzed, it should be placed in a plastic bottle, preserved by the addition of 1 mL/liter of concentrated sulfuric acid (sp gr 1.84), and stored in a frozen condition. The ammonia content in the sample will remain for up to 30 days.

Limits of Detection

The colorimetric determination of ammonia has a detection limit of 0.50 mg/liter with an uncertainty of ±0.03 mg/L.

A-2 BROMIDE AND IODIDE (STORET NO. 71870)

Summary of Method

The determination of bromide and iodide consists of two separate experiments. The iodide is first determined in the sample, and then a second experiment determines the combined iodide and bromide. The bromide content of the sample is calculated from the difference between the iodide and the combined iodide and bromide determination.

The iodide in the sample is oxidized to iodate with saturated bromine water in an acid buffer solution. The excess bromine is destroyed by the addition of sodium formate. Potassium iodide is added to the sample solution with the resulting liberated iodine being equivalent to the iodate initially formed in the oxidiation step. The liberated iodine is determined by titration with sodium thiosulfate.

In a second sample, iodide and bromide are oxidized to iodate and bromate with calcium hypochlorite. The iodine liberated by the combined reaction products is measured after destruction of the excess hypochlorite and addition of potassium iodide.

Interferences

Iron, manganese, and organic matter interfere with the above methods. Treatment of the initial samples with calcium oxide removes the interferents.

Sampling

Collect samples in accordance with American Society for Testing and Materials methods D1192 and D3370.

Limits of Detection

The titrimetric determination of iodide and bromide has a detection limit in the mg/liter range.

A-3 CARBONATE AND BICARBONATE (ASTM D513-71)

Summary of Method

Carbon dioxide is liberated by acidifying and heating the sample in a closed system which includes a condenser, a gas scrubber, a CO_2 absorber, an expansion bladder, and a gas-circulating pump. The CO_2 gas is absorbed in a barium hydroxide solution and the excess hydroxide is titrated with standard acid. The concentrations of the carbonate species are determined from the pH and total CO_2 values.

Interferences

Carbon dioxide can be lost from solution during transit and storage of samples.

Any volatile acid, base, or barium precipitate not removed by the scrubbing solution will interfere.

Hydrogen sulfide is an interferent but is removed with the iodine scrubbing solution.

Sampling

Collect samples in accordance with American Society for Testing and Materials methods D1066, D1192 and D3370.

Limits of Detection

The titrimetric determination of total CO_2 has a detection limit in the mg/liter range with a precision of 0.25 mg/liter.

A-4 CHLORIDE (STORET NO. 00940)

Summary of Method

The sample solution is adjusted to pH 8.3 and then titrated with mercuric nitrate solution in the presence of diphenyl carbazone-bromophenol blue indicator. The persistence (10 sec) of the blue-violet mercury complex color indicates the end point for the titration.

Interferences

Anions and cations normally in surface waters do not interfere. Sulfite must be eliminated (addition of H_2O_2).

Sampling

Collect samples in accordance with American Society for Testing and Materials methods D1066 and D3370.

Limits of Detection

The titrimetric determination of chloride has a detection limit in the mg/liter range.

A-5 CYANIDE (STORET NO. 00720)

Summary of Method

The sample is refluxed with a solution consisting of H_2SO_4 and Cu_2Cl_2. Hydrogen cyanide gas is liberated and absorbed in NaOH solution. Either a colorimetric or titrimetric procedure may be used for the determination of cyanide.

The colorimetric procedure calls for the neutralization of the absorption solution with acetic acid to pH 6.5 - 8.0 and the addition of 0.2 ml of chloramine-T solution. The solution absorbance is measured at 620 nm after twenty minutes. This procedure is recommended for solutions where the cyanide concentration is 1 mg/liter or less.

For the titrimetric procedure, the absorption solution is titrated with $AgNO_3$ using Rhodamine B as the indicator.

Interferences

Interferences include substances which contribute to color or turbidity changes. The presence of cyanate or thiocyanate or the presence of organic nitrogen compounds also interferes.

Some organic cyanide compounds like nitriles decompose under distillation. Aldehydes convert cyanide to nitrile.

Sampling

Collect the sample in accordance with American Society for Testing and Materials methods D1192 and D3370. If the sample cannot be analyzed immediately, stabilize it by the addition of NaOH solution to a pH of 12 or more and store it in a closed plastic bottle. If chlorine is present, add ascorbic acid as soon as the sample is collected.

Limit of Detection

Titrimetric and spectrometric determinations of cyanide have detection limits of 1 mg/L and 0.02 mg/L, respectively.

A-6 FLUORIDE (STORET NO. 00951)

Summary of Method

The pH of the sample is adjusted to 5.2 - 5.5 with 0.5 N H_2SO_4. Carbon dioxide is removed from solution by heating on a hot water bath. The pH of the sample is adjusted to 6.3 with a buffer solution of 1M sodium citrate - citric acid - 0.2M KNO_3. Fluoride is determined using a specific ion electrode and standard addition methods.

Interferences

Metals such as Fe and Al can form complexes with F^-. These interferences are minimized by the addition of the citrate buffer solution, which preferentially complexes the metals, and by controlling the pH.

Sampling

Collect samples in accordance with American Society for Testing and Materials methods D510, D1192 and D1496. Sample are preserved in a plastic container and stored at 4°C.

Limits of Detection

The specific ion electrode determination of fluoride has a detection limit of 1 mg/liter with an uncertainty of ±0.1 mg/L.

A-7 NITRATE (STORET NO. 00620)

Summary of Method

Nitrate ion reacts with brucine in a strong sulfuric acid solution to develop a yellow color. The color is measured at 410 nm but the Beer-Lambert relationship dces not hold for this system. A plot of absorbance versus concentration produces a smooth curve which replaces the Beer-Lambert relationship. The rate of color development varies directly with temperature and the intensity varies inversely with the temperature. Samples containing 1 to 50 mg/liter of NO_3^- ion can be analyzed by this method. Samples with large concentrations of NO_3^- ion must first be diluted.

Interferences

Chlorine can have an interference of up to 5 mg/liter but may be eliminated by the addition of sodium arsenite.

Strong oxidizing or reducing agents will cause interferences.

Nitrite can have an interference of up to 7 mg/liter but is eliminated by the sulfanilic acid in the brucine reagent solution.

Organic matter in the sample may interfere by increasing the absorbance readings at 410 nm. The problem comes about because concentrated sulfuric acid will char the organic molecules. This problem can be eliminated by pretreatment with aluminum hydroxide and specially treated activated carbon.

Sampling

Collect samples in accordance with American Society for Testing and Materials method D1192 and D3370.

Limit of Detection

The spectrometric determination of nitrate has a detection limit in the mg/liter range.

A-8 NITRITE (STORET NO. 00630)

Summary of Method

Nitrite is measured spectrophotometrically following diazotization with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride. The resulting azo dye is measured at 540 nm. The method is applicable to samples containing 0.01 to 1.0 mg/L. Nitrate is determined in a separate aliquot of the sample following reduction to nitrite using a column of granular copper/cadmium mixture. Nitrate is calculated from the difference in nitrite concentrations of the two solutions.

Interferences

Interferences due to high concentrations of metals (e.g., Fe and Cu) may be eliminated by complexing with EDTA. Turbid samples should be filtered. Samples containing oil or grease must be pre-extracted if this nitrite/nitrate procedure is employed.

Sampling

Collect the samples in accordance with American Society for Testing and Materials method D1066, D1192, and D3370.

Limit of Detection

The spectrometric determination of nitrite has a detection limit of 0.01 mg/liter.

A-9 ORTHOPHOSPHATE (STORET NO. 00665)

Summary of Method

A solution of ammonium molybdate-vanadate is added to the sample producing the yellow color of molybdovanadophosphoric acid. The color intensity is proportional to the orthophosphate concentration of the sample. The yellow color is measured at 400 nm. This method is recommended for samples where the concentration of othophosphates is 1 to 10 mg/liter. For more dilute samples the colorimetric ascorbic acid reduction method should be applied.

Interferences

High concentrations of the ferric ion will interfere with this method as will other highly colored species.

Sampling

Collect samples in accordance with American Society for Testing and Material methods D1066, D1192 and D3370. If analysis cannot be performed immediately, preserve by the addition of 40 mg of mercuric chloride per liter of sample and store at 4°C.

Limits of Detection

The spectrometric determination of othophosphates has a detection limit in the mg/liter range.

A-10 SULFIDE (STORET NO. TOTAL 00745)

Summary of Method

After the sample is acidified, sulfide is stripped from the sample with an inert gas and collected in a zinc acetate solution. The stripped sulfide forms a zinc sulfide suspension in the collection solution. The addition of excess iodine to the suspension causes the sulfide to react under acidic conditions. Thiosulfate is used to measure the unreacted iodine to determine the quantity of iodine consumed by sulfide.

Interferences

Reduced sulfur compounds, such as sulfite, thiosulfate, and hydrosulfite decompose in acid and will cause erratic results.

Volatile iodine-consuming substances give high results.

Samples must be taken with a minimum of aeration to avoid oxidation of sulfide.

Sampling

Collect samples in accordance with American Society for Testing and Materials methods D1066, D1192 and D3370. If analysis cannot be performed immediately, preserve with zinc acetate.

Limits of Detection

Precision and accuracy for this method have not been determined.

A-11 SULFITE (STORET NO. 00740)

Summary of Method

The sample is taken in a tube of special design which excludes air until the sulfite has been reacted with a solution containing HCl, KI, and KIO_3. The excess iodine chloride is determined by titration with thiosulfate using a deadstop endpoint-indicating apparatus. This method is recommended for sample concentrations of 0.1 to 6 mg/liter.

Interferences

Reducing agents such as sulfides and certain heavy-metal ions react with iodine chloride.

If nitrite ion is present, it will oxidize sulfite when the solution is acidified.

Sampling

Collect samples in accordance with American Society for Testing and Materials method D1192 and D3370.

Limits of Detection

The titrimetric determination of sulfite has a detection limit in the 0.1 mg/liter range.

A-12 SULFATE (STORET NO. 00945)

Summary of Method

There are three basic methods for the determination of sulfates: gravimetry, turbidimetry and titrimetry. Gravimetry is a primary measure of sulfate ion in all types of water but it is time consuming and has a lower sensitivity. Turbidimetry is the most sensitive and titrimetry is the fastest.

For the gravimetric method, sulfate ion is precipatated and weighed as barium sulfate after removal of silica and other insoluble matter by filtration.

For the turidimetric method, sulfate ion is converted to a barium sulfate suspension. Glycerin and sodium chloride solutions are added to stabilize the suspension and minimize interference. The turbidity is determined on a spectrophotometer and compared to standard sulfate solutions.

For the volumetric method, sulfate ion is titrated in an alcoholic solution under controlled acid conditions with a standard barium chloride solution. Thorin is employed as the indicator with a color change of yellow to pink.

Interferences

Gravimetric interferences are caused by other substances being occluded or adsorbed on the barium sulfate. Sulfites and sulfides may oxidize and precipitate as sulfate. Turbidimetric interferences are caused by insoluble suspended matter. Volumetric interferences are usually caused by cations and anions which may coprecipitate. Most interfering cations are removed by ion exchange columns.

Sampling

Collect samples in accordance with American Society for Testing and Materials methods D1066, D1192 and D3370.

Limits of Detection

The gravimetric method has a detection limit of 10 mg/liter.

The turbidimetric method has a detection limit of 2 mg/liter.

The volumetric method has a detection limit of 1.5 mg/liter if ion-exchange chromatography is employed, 5 to 10 mg/liter otherwise.